# ANALYTICAL ABSTRACTS



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# ANALYTICAL ABSTRACTS

## 1.—GENERAL ANALYTICAL CHEMISTRY

2930. **Review of industrial applications of analysis, control and instrumentation.** (*Anal. Chem.*, 1955, **27** [4], Part II).—This review includes the following contributions. **Automatic operations.** G. D. Patterson, jun. (574–589). **Natural and synthetic rubbers.** N. Bekkedahl and M. Tryon (589–598). **Petroleum.** H. Levin (599–606). **Coatings.** R. W. Stafford and W. G. Deichert (606–611). **Ferrous metallurgy.** H. F. Beeghly (611–614). **Non-ferrous metallurgy.** M. L. Moss (614–623). **Food.** J. R. Matchett and H. W. von Loesecke (623–632). **Fertilisers.** G. L. Bridger (632–636). **Pharmaceuticals and natural drugs.** M. M. Marsh and W. W. Hilty (636–653). **Pesticides.** J. L. St. John (654–660). **Solid and gaseous fuels.** H. T. Darby (660–671). **Essential oils and related products.** E. Guenther and E. E. Langenau (672–677). **Clinical chemistry.** R. M. Archibald (677–679). **Water analysis.** S. K. Love and L. L. Thatcher (680–690). Numerous references are given.
N. E.

2931. **Buoyancy of beam balances in relation to their construction.** H. Ulbricht (*Z. anal. Chem.*, 1955, **145** [3], 161–175).—A detailed mathematical investigation is given of the importance of air buoyancy on accurate weighing on single- and two-armed balances. Corrections for buoyancy, calculated from formulae, curves and examples, are given, showing that inadmissably large errors may occur in both analytical and less accurate weighing.
P. Haas

2932. **A note on the estimation of error in slope-ratio assays arranged in randomised blocks.** P. M. Clarke (*Analyst*, 1955, **80**, 396–397).—It is pointed out that, in multiple slope-ratio assays arranged in randomised blocks with no intra-block replication, the blocks × regression interaction must be eliminated in obtaining an estimate of error variance from the blocks × treatments interaction. In three out of four examples quoted for vitamin $B_{12}$, the blocks × regression mean square was highly significant, and the estimate of error variance obtained by pooling the remaining interaction mean squares was at least 80 per cent. lower than that given by the mean square for all the interactions. B. J. Walby

2933. **1-(2-Pyridylazo)-2-naphthol as a possible analytical reagent.** K. L. Cheng and R. H. Bray (*Anal. Chem.*, 1955, **27** [5], 782–785).—1-(2-Pyridylazo)-2-naphthol in methanol gives coloured chelates or lakes, soluble in amyl alcohol or $CCl_4$, with 20 heavy-metal cations, unless EDTA is present. The green ppt. formed with $PdCl_4''$ and $Co'''$ are characteristic of these ions. Details are given for the use of the reagent as an indicator in the EDTA titration of $Zn''$, $Cd''$ and $Cu''$, in which the alkaline-earth cations do not interfere, and for the colorimetric determination of $Zn''$, $Cu''$, $Ni''$ and $Co'''$. D. A. Pantony

2934. **New complexing agents.** R. P. Lastovskiĭ, Yu. I. Vaĭnshteĭn, N. M. Dyatlova, V. Ya. Temkina and I. D. Kolpakova (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 128–131).—By the condensation of Na chloroacetate with hexamethylenediamine or with benzhydrylamine in aq. NaOH solution two new complexing agents, hexamethylenediaminetetra-acetic acid and benzhydrylaminediacetic acid, are obtained. The behaviour of these compounds towards 17 cations is described. G. S. Smith

2935. **Analysis for industry. [Uses of sodium tetraphenylboron. I.]** A. Sykes (*Ind. Chem. Mfr*, 1955, **31**, 245–247).—The preparation and stability of Na tetraphenylboron solutions are discussed. Three methods of determining K are described, based on the pptn. of K tetraphenylboron (solubility product = $3{\cdot}3 \times 10^{-8}$ at 25° C), dissolving in acetone and treatment with standard $AgNO_3$ solution. Potassium may also be determined in the presence of $NH_3$ by using formaldehyde and excess of NaOH. Certain alkaloids and org. N-containing bases, *e.g.*, atropine, phenazone, amidopyrine and pyridine, may be determined with the reagent in the presence of acetic acid and $Al(NO_3)_3$. Three methods of determining K in wine are given and by a suitable combination of these the K-, $NH_3$- and N-containing org. bases in wine can be calculated. D. R. Peck

2936. **Analysis for industry. [Uses of sodium tetraphenylboron. II.]** A. Sykes (*Ind. Chem. Mfr*, 1955, **31**, 305–307).—The analytical applications of Na tetraphenylboron (**I**) are further reviewed (*cf. Anal. Abstr.*, 1955, **2**, 2935), and include the microvolumetric determination of K in mixtures of K and Na, coal ash and plants; the determination of K and triethanolamine in mixtures; and the identification of analgesics and alkaloids by determining the m.p. of the **I** derivative in conjunction with the eutectic temp. of the sample with acetanilide or phenacetin. S.C.I. Abstr.

2937. **Micro-drop method for identifying cations by the method of Weisz.** C. A. Bank and W. van der Eijk (*Chem. Weekbl.*, 1955, **51** [20], 351–356).—The method of Weisz for separating Hg, Pb, Bi, Sb, Sn, As, Cu, Cd, Fe, Co, Ni, Cr, Mn, Zn and Al is described. The filter-paper spotted with the solution under test is treated with $H_2S$ and then with 0·1 *N* HCl, to give ring I containing Fe, Ni, Cr, Mn, Zn, Al and Cr. This ring is divided into seven portions and each portion is tested with a reagent specific for each element. The spot is then oxidised with Br and washed with aq. $NH_3$ soln., to give ring II, containing Cu and Cd. Ring II is divided into two parts: Cu is tested for by rubeanic acid and Cd by treatment with $H_2S$ followed by KCN and $AgNO_3$. The remaining spot is treated with hot $(NH_4)_2CO_3$; this removes As, which is tested for in ring III. The spot, which now contains Hg, Pb, Bi, Sn and Sb, is treated with $(NH_4)_2S_x$, which gives ring IV containing Sb and Sn, while Pb, Bi and Hg remain in the spot. The usual spot reagents are used to

detect these elements. The method has the advantage of rapidity and of requiring very little of the test solution. A. J. MEE

2938. **Separation of the [metals of the] hydrogen sulphide group by paper chromatography.** E. Pfeil with G. Ploss and H. Saran (*Z. anal. Chem.*, 1955, **146** [4], 241–243).—Butanol saturated with HCl (3·4 to 3·5 *N*) was the best solvent for the ions of the $H_2S$ group metals; Schleicher and Schüll 2043b paper was used. First treat the chromatogram with KI (0·2 per cent.) and then develop with conc. HCl. Heat to fuming with aq. $NH_3$ soln. till the As spot has disappeared. Add $(NH_4)_2S$ to identify Hg, Cd, Bi, Pb, Cu and Ag. Dry, add quercitin soln. and dry again to develop Sn. Sensitivity limits are given. R. STERN

2939. **One-colour acid - alkali indicators.** G. I. Mikhallov (*Zavod. Lab.*, 1955, **21** [2], 156–162).—A review of the literature is given with descriptions and properties of 30 indicators. An indicator, obtained by mixing equal vol. of 0·1 per cent. alcoholic solutions of 2:4:2′:4′:2″:4″-hexamethoxytriphenylmethanol and thymolphthalein, which is red below pH 4·6, colourless from pH 4·6 to 9·3 and dark blue from pH 9·3 to 14, is described. G. S. SMITH

2940. **Argentimetric indicators.** N. F. Dobrovol'skiĭ (*Soobshch. Nauch. Rabot. Vsesoyuz. Khim. Obshch. im. Mendeleeva*, 1953, [3], 12–17; *Referativnyĭ Zh., Khim.*, 1954, Abstr. No. 25,734).—Aniline blue and Alkali blue were used for determining I′ and Ag·. Aniline blue is employed as a $10^{-3}$ *M* soln. in 50 per cent. ethanol. Near the equiv. point the suspension becomes greenish blue. The minimum determinable concn. of I′ and Ag· is 0·02 *N*. The determinations can be carried out at pH 1·4 to 9·4, but the most favourable range is 3 to 8·8. Small quantities of $HNO_3$ and NaOH do not interfere. For the titration of 20 to 25 ml of I′ with $AgNO_3$, 2·5 to 14 ml of indicator are suitable. The error of determination is from − 0·11 to − 0·5 per cent. Titration of Ag· with KI soln. can be carried out only in artificial light. The optimum amount of indicator is 4 ml per 20 ml of titrated soln. The error of determination is 0·15 to 0·20 per cent. Alkali blue is used as a 0·1 per cent. soln. in 50 per cent. ethanol. The minimum determinable concn. of I′ is 0·015 *N*. The optimum quantity of indicator per 20 ml of titrated soln. is 4 to 20 ml for 0·1 *N* KI and 4 to 5 ml for 0·05 *N*, and the pH range is 2·1 to 9·3. Free $HNO_3$ and NaOH do not interfere. For micro-determinations of KI, 0·3 to 0·5 ml of indicator per 2 ml of titrated soln. is used. The error of determination is ± 0·6 per cent. Titration of Ag· with KI solution is reliable only in electric light. Alkali blue permits the determination of Cl′ and I′ when present together. First I′ is titrated to the transition of violet - blue to green - blue, then the pptn. of Cl′ is complete when the soln. is clear. The average error in the determination of I′ is < 0·7 per cent. CHEM. ABSTR.

2941. **Stable starch solutions for iodimetry.** A. C. Holler (*Anal. Chem.*, 1955, **27** [5], 866).—A stable and sensitive starch indicator is made by dissolving starch (5 g) in formamide (100 ml) at 100° to 110° C. The indicator has very satisfactory properties. D. A. PANTONY

2942. **Quantitative characteristics determining the use of complex compounds in volumetric analysis.** K. B. Yatsimirskiĭ (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 94–99).—In complexim etric titrations the max. attainable accuracy is determined by the value of the instability const. of the complex formed and the initial concn. of the reacting substances. An index of the accuracy of a titration, p$T$, is defined as − log ratio of concn. at equivalence point to initial concn. of a substance; thus with p$T$ = 3, the accuracy is 0·1 per cent. With a reaction of the type M + A = MA, $pC_0 + 2pT = pK$, where $pC_0$ is − log initial concn. of one of the substances and p$K$ is − log dissociation const. or − log instability const. of MA. Hence for titrations of 0·1 *M* solutions with an accuracy of 0·1 per cent., p$K$ must be > 7. When a complex $MA_n$ is formed, $pK_n$ must be > 4$n$ + 3. These conditions are applicable to many titrations, *e.g.*, those involving cyano complexes of metals, thiosulphate complexes of Ag and Hg, ethylenediamine complexes of Cu and Ni, and ethylenediaminetetra-acetic acid complexes. With the reaction M + HA = MA + H·, $pC_0 + 2pT = pK - pK_D + pH$, where $pK_D$ is − log dissociation const. of HA. For an accuracy of 0·1 per cent. and initial concn. 0·1 *M*, the min. pH is given by $pH_{min.} = pK_D - pK + 7$. With $H_2A$ instead of HA the equation is $pH_{min.} = \frac{1}{2}(\Sigma pK_D - pK + 7)$, where $\Sigma pK_D$ is the sum of the indexes of the dissociation const. of $H_2A$. From this equation the min. pH for titrations with ethylenediaminetetra-acetic acid are calculated. Thus with $Mg^{··}$ (p$K$ of complex 8·7), $pH_{min.}$ = 9·3, and with $Zn^{··}$ (p$K$ 16·7) $pH_{min.}$ = 3·3. A similar equation applicable to masking is also derived, and applied to complexes of Zn. Examples of the use of unstable complexes in other cases are discussed. G. S. SMITH

2943. **High-frequency titration. II. Change in electrical characteristics of solutions during titration.** V. A. Zarinskiĭ and D. I. Koshkin (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 110–118).—An account is given of a development of the work previously described (*Anal. Abstr.*, 1954, **1**, 2275). With high-frequency titration, as with the usual conductimetric titration, the measured effects are determined by changes in ohmic resistance of the solution and not by capacity changes. A 36-Mc.p.s. generator is described for titrations of acid - alkali in alcohol - water solutions of synthetic resins and plasticisers, for determinations of phenols, etc. G. S. SMITH

2944. **Cryoscopic titration.** M. Usanovich, T. Sumarokova and Yu. Nevskaya (*Dokl. Akad. Nauk, SSSR*, 1954, **98** [4], 617–618).—Curves connecting depression of f.p., $\Delta t$, of solutions with vol. of added standard solutions of reagents consist of two branches, intersecting at $\Delta t$ = zero when an insol. addition compound is formed, or at $\Delta t$ > zero when the compound is soluble. Examples are the titration of dichlorobenzene solutions of pyridine, dioxan or *p*-benzoquinone with $SnCl_4$, which gives an insol. compound with pyridine, and sol. compounds with dioxan and *p*-benzoquinone. R. TRUSCOE

2945. **Effect of particle size on the characteristics of silicic acid chromatographic adsorbent.** E. W. Malmberg (*Anal. Chem.*, 1955, **27** [5], 840–842).—The quality of chromatographic separation of 2:4-dinitrophenylhydrazones on silica gel diluted with kieselguhr (0·5 part) is investigated. In general, grinding to − 300 mesh and heating the gel to 200° C gives the best results. D. A. PANTONY

2946. **Sorption chromatography of polar substances on polyamides.** V. Carelli, A. M. Liquori and A. Mele (*Nature*, 1955, **176**, 70–71).—Examples of the use of polyamides as absorbents for chromatographic separation of polar substances are reported. A Tiselius - Claesson apparatus of the *L.K.B.* type was used. A soln. in *cyclo*hexane of the compounds to be separated was forced through a short column of tightly packed powder of poly(hexamethylene adipamide). The change in refractive index in the eluate was determined interferometrically, according to the method of Claesson. The chromatograms had sharp fronts. When a solution of 2:5-xylenol (m.p. 74° C, b.p. 211° C) and 2:6-xylenol (m.p. 49° C, b.p. 212° C) was absorbed at the top of the column and a solution of 3:5-xylenol (m.p. 68° C, b.p. 219° C) was then forced through the column, the first two isomers were displaced by the third, and a complete separation was achieved. The extent of absorption followed the sequence 2:6-xylenol < 2:5-xylenol < 3:5-xylenol, and in other examples *n*-hexoic acid < butyric acid < propionic acid, and *o*-cresol < *m*-cresol < phenol. O. M. WHITTON

2947. **New technique for circular chromatography.** J. Carles (*Bull. Soc. Chim. Biol.*, 1955, **37** [4], 521–524).—The apparatus consists of a crystallising dish containing a layer of aqueous phase in which is standing a narrow bottle filled with solvent and fitted with a capillary tube reaching from near the bottom of the bottle through the narrow neck up to a short distance below the level of the top of the dish. A piece of chromatographic filter-paper, of circumference slightly greater than that of the dish, is placed on the dish, and from 20 to 100 cu. mm of the solution, containing from 5 to 20 per cent. of sugar, are put on the centre of the paper. As soon as the paper is dry, the centre is pierced by a fine needle long enough to dip into the open end of the capillary projecting from the bottle, and the dish is then covered with a sheet of glass. If a two-phase solvent is used, the active phase is placed in the bottle while the water is put into the dish. The method can be used for all sorts of substances and is very rapid. A chromatogram of 10 cm in diameter can be produced from chlorophyll in 10 min. Sugars having a low $R_F$ value show wide separation. The distances in cm for fructose, sucrose, raffinose and stachyose by this method are 4·8, 3·75, 2·25 and 1·75, respectively, as compared with 2·3, 1·4, 0·5 and 0·3 by the ordinary chromatographic method. P. HAAS

2948. **Phosphoric acid as a complexing eluent in ion-exchange chromatography.** J. A. R. Genge, A. Holroyd, J. E. Salmon and J. G. L. Wall (*Chem. & Ind.*, 1955, [13], 357–358).—Various acids have been tested as complexing eluents for the ion-exchange chromatographic separation of tervalent Al and Fe from bivalent Cd, Co, Cu, Mg, Mn, Ni and Zn. Results showed that at any pH between 0·25 and 0·75, (*a*) the proportion of $Fe^{\cdot\cdot\cdot}$ removed from the resin decreased in the order phosphoric > sulphuric > hydrochloric > nitric > perchloric acid, but that for the zinc form of the resin the proportion of metal removed decreased in the order hydrochloric > phosphoric = perchloric acid; and (*b*) the proportion of metal initially on the resin which passed into solution at equilibrium decreased in the order $Fe^{\cdot\cdot\cdot} > Al^{\cdot\cdot\cdot} > Zn^{\cdot\cdot} > Mn^{\cdot\cdot}$ for phosphoric acid. Results of a number of separations are given. The acids were passed through a column (8 in. × ¼ in.) containing 22 to 30-mesh resin, at 100 ml per hr. Phosphoric acid (≃ 280 ml, pH 0·5) was used to elute the $Fe^{\cdot\cdot\cdot}$, and HCl (250 ml, 3 *N*) to remove $Cu^{\cdot\cdot}$ and $Mn^{\cdot\cdot}$. These clear-cut separations should be of use in analytical and purification processes. O. M. WHITTON

2949. **Contributions to the theory of gradient elution analysis.** B. Drake (*Ark. Kemi*, 1955, **8** [1], 1–21).—The migration of a test substance through a sorbent is computed as far as possible in terms of various forms of concentration gradient of an eluting mixture when the gradient substance has a linear isotherm. When the substance has a curved isotherm the results are illustrated graphically. The sharpening of zones that is obtained by gradient elution analysis is considered as an advantage to set against the disadvantage of the zones being brought closer together. Methods of calculation for planning elutions are suggested and the dependence of gradient equations on the volumes and shapes of mixing chambers is discussed. (24 references.) E. J. H. BIRCH

2950. **The importance of micro-chemical methods for spectral analysis.** G. Gorbach (*Mikrochim. Acta*, 1955, [2–3], 336–344).—Micro-apparatus that is universally applicable to preliminary purification of spectrographic samples is reviewed. Solutions of known concn., even from only very small amounts of samples, are accurately prepared by using precision pipettes. Membrane micro-burettes and micro-capillary pipettes with capacities of 10 to 100 μl are useful in the quant. evaluation of emission spectral analyses, especially in transferring the samples to the electrode carbons. The sensitivity of the detection of several elements is increased by several powers of ten by using org. complexing agents, *e.g.*, dithizone and oxine, and by preheating the electrode carbons to 110° C in a suitable block to diminish the depth to which the sample penetrates the carbon. For absorption spectrophotometry a newly-developed capillary photometer is recommended for analysis of elements of low spectral sensitivity; this permits high accuracy of measurement when using a capillary 100 mm in length. D. R. GLASSON

2951. **A solution method of spectrographic analysis.** D. V. Evans and D. Johnston (*Metallurgia*, 1955, **51** [307], 261–262).—The advantages of a solution method of spectrographic analysis and the known techniques of sparking solutions are discussed. An alloy solution delivered in the form of a fine spray through a hollow graphite electrode forming the counter electrode of a graphite - graphite spark-gap gave well-resolved spectral lines, but severe incrustation of the electrodes occurred. Spraying the liquid directly into the spark-gap also gave well-resolved spectral lines. This method was examined using a Lundegårdh atomiser through a reducing valve under a nitrogen cylinder at a pressure of 30 lb per sq. in. Reproducibility tests were carried out and the conditions standardised. The following results were obtained on a brass sample containing 27·66 per cent. of Zn, taking the mean of three determinations: range 27·16 to 28·30 per cent. of Zn, standard deviation ± 0·23. Spectrographic and chemical analyses of various samples of commercial brass are compared. G. C. JONES

2952. **A general method of spectrochemical analysis of non-conducting materials.** J. Beintema and J. Kroonen (*Mikrochim. Acta*, 1955, [2–3], 345–357).—The d.c. arc is a good light source for spectrochemical analysis of non-conductors when

the fractional volatilisation of the sample is diminished and the temp. in the arc column is constant. This is achieved by thoroughly mixing the sample with $Li_2CO_3$ (4 to 40 parts) and a large excess of graphite powder (20 to 200 parts). The homogeneous mixture is charged into special graphite electrodes and covered with a layer of graphite powder 1 mm thick; Harvey-type electrodes are modified by reducing the diameter to 2 mm, which improves the centralisation of the electric discharge. Calibrations can be made with synthetic samples, since the influence of differences in the composition of the main constituents and in the chemical and physical structure is largely eliminated. The determination of Al, Ca, Si, Fe, Na and Pb is effected with an accuracy generally better than ± 10 per cent. D. R. GLASSON

2953. **Results of intensity determinations using the s.p.d. scale.** J. A. M. Dikhoff and N. W. H. Addink (*Mikrochim. Acta*, 1955, [2–3], 257–264).—Light intensities are determined visually by the standard paper density (s.p.d.) scale. The basic correction of the accuracy of the method and other factors which may affect measurements with the s.p.d. scale are discussed. Since the spectral lines are not equally blackened, as are the normal s.p.d. scale lines, comparison is facilitated by using a standard scale of lines with a spectral-line-like blackened profile. D. R. GLASSON

2954. **Reduction of errors in quantitative arc-spectral analysis by weighting the logarithms of the intensity ratios.** G. Holdt (*Mikrochim. Acta*, 1955, [2–3], 286–297).—The photographically measured intensity relations of the supplementary and reference lines, when represented as the difference of the logarithms of their intensities, give the smallest scattering of the intensity relationships only when the Y-errors of both lines in the statistical averages are identical; this constitutes the most suitable method of estimation. When they differ, the scattering is minimised by applying a readily determined no. as a weighting factor to the reference line. The "weighted Y-difference" thus obtained is a generalisation of the customary "simple Y-difference" (wt. plus one). It eliminates the systematic error occurring in the intensity ratio and considerably diminishes the error in the quant. analysis, if the residual accidental proportionate errors are slight. In contrast to spark-like procedures, different values of the Y-error appear in the arc; this is discussed. D. R. GLASSON

2955. **Analytical applications of the near infra-red by means of the Beckman u.v. spectrophotometer.** M. P. Groenewege and H. A. van Vucht (*Mikrochim. Acta*, 1955, [2–3], 471–480).—Absorptions of the second harmonic over the vibration of the CH, OH and NH groups are measured relatively easily by using the Beckman u.v. spectrophotometer. A layer thickness of 1 cm is required for liquids and 10 cm for solids in 10 per cent. soln. in $CCl_4$ or $CS_2$. It is possible to detect OH, NH, aromatic CH, paraffinic CH and sometimes olefinic and "hyperaromatic" CH (pyrrole, thiophen). Certain anomalies are exhibited by compounds containing O, *e.g.*, ethers and aldehydes. The "varial index" is proposed as a practical value for characterising aromatic - aliphatic products, since this index represents the ratio of the max. extinctions of the aromatic to those of the aliphatic CH bonds. D. R. GLASSON

2956. **Industrial applications of infra-red gas analysis.** J. O. Lay (*Metallurgia*, 1955, **51** [304], 109–112).—A wide range of compound gases are detected and evaluated in gaseous mixtures by measuring their i.r. absorption characteristics; the heat loss at appropriate wavelengths, which results from the passage of i.r. radiation through the mixture, is directly related to the proportion of any specific compound present. Suitable apparatus, in which the sensitivity can be adjusted to cover the range 0 to 100 per cent., is described. Filters, generally chambers containing an interfering gas, remove unwanted radiation. Non-absorbent simple gases are often chemically convertible into i.r.-absorbent compounds. Methods for determining more than one component are mentioned. Industrial applications include the determination of $CH_4$ and $CO_2$ in mines; hydrocarbons and CO, $CO_2$ and $SO_2$ in fuel control; HCN, $NH_3$ and H (indirectly as $H_2O$) in metallurgy; $N_2O$ in testing vacuum equipment; $H_2O$ in moisture control; $CO_2$ and $SO_2$ in the determination of C and S in steel; identification and measurement of organic compounds such as acetone, higher alcohols and benzene deriv. in ordinary atm., as in the control of industrial solvent recovery or extraction plants. D. R. GLASSON

2957. **Polarography with platinum micro-electrodes in fused salts.** E. D. Black and T. De Vries (*Anal. Chem.*, 1955, **27** [6], 906–909).—The application of polarography to fused salts is described. Platinum micro-electrodes and automatic recording are used and the effects of variations in polarisation rate, area of electrode, speed of rotation of electrode, and temperature have been studied. Linear relationships between wave height and mole fraction were obtained for dilute solutions of the chlorides of Cd, Co, Ni, Pb and Zn and potassium chromate in a LiCl - KCl eutectic between 380° and 450° C. In a melt of the nitrates of Li, Na and K as solvent with rotating spherical platinum or silver micro-cathodes, a linear relationship between wave height and concn. of $CuSO_4$ was observed. K. A. PROCTOR

2958. **Nomogram for determining the characteristics of capillaries in polarography.** D. P. Shcherbov (*Zavod. Lab.*, 1955, **21** [2], 246–247).—The equation for the capillary is expressed as $K = 0{\cdot}129\ m_0^{\frac{1}{3}} n^{-\frac{1}{3}}$, where $n$ and $m_0$ are the no. of drops and the weight of Hg, respectively, passing through the capillary in 1 min. The nomogram consists of three parallel straight lines representing $n$ 10 to 300, $m_0$ 0·05 to 1·50, and $K$ 1·0 to 8·0, and graduated logarithmically. G. S. SMITH

2959. **Polarographic differential titration.** N. Ya. Khlopin, L. G. Geĭn and A. A. Bakhareva (*Zavod. Lab.*, 1955, **21** [2], 135–140).—A method of dead-stop titration is described. The current between two similar platinum electrodes is compensated after each addition of titrant and the polarisation curve is plotted. Examples of the use of the method are given. G. S. SMITH

## 2.—INORGANIC ANALYSIS

2960. **Precipitation of metals with monosubstituted dithiocarbamates.** E. Gagliardi and W. Haas (*Mikrochim. Acta*, 1955, [4], 864–878).—Conditions controlling the pptn. of metal ions with the ammonium salts of *o*-, *m*- and *p*-aminophenyldithiocarbamate, respectively, have been studied,

including the possibility of extracting the ppt. with org. solvents and of the specific pptn. of a metal ion at different pH values. Generally, the ppt. have low solubility and can be easily filtered off; qual. separations are most effective at pH $< 4$. The position of the $NH_2$ group appreciably affects the course of pptn.; a very sensitive colour test for $CrO_4''$ can be obtained with the *o*-aminophenyldithiocarbamate. The elements in groups IA to IVA, VIIB and VIIIB of the Periodic Table do not react with the dithiocarbamates. W. J. BAKER

2961. **Polarographic behaviour of sodium diethyldithiocarbamate.** J. Davis, A. J. Easton and J. Freezer (*Chem. & Ind.*, 1955, [10], 241–242).—A polarographic method for determining metals is described. The reduction in wave height of sodium diethyldithiocarbamate in a buffer solution when it forms a complex with a metal ion, *e.g.*, $Fe^{'''}$, Co, Cu, Zn, Mn, $Hg^{''}$, Ni, Ag, Ba, Bi, Mg, Cd, Au, Pb, Mo, As, V, W, Ca, Sb, Al and Te (but not Sn, Ce or Cr), is measured and then compared with a calibrated curve. The base solution is prepared by adding 20 g of KCl and 100 g of ammonium acetate to 240 ml of aq. $NH_3$ soln. (1 + 4), and making up to 1 litre. Alternatively, the equivalent quantities may be added to the solution of metal under test. A solution of 0·1 g of sodium diethyldithiocarbamate in 1 litre of water is prepared. If the base solution is used, 25 ml are placed in a 50-ml calibrated flask and 10 ml of the reagent solution are added. An aliquot of the test solution is added, any appreciable quantity of acid or alkali having been neutralised with dilute aq. $NH_3$ soln. or HCl. The wave recording is started at $-$ 1·1 V *vs.* the mercury-pool electrode and is continued until the full development of the wave. A blank is prepared as above, but without adding the test solution. The decrease in wave height is then compared with a calibrated curve. O. M. WHITTON

2962. **The quantometric analysis of light metals.** G. Winkler (*Mikrochim. Acta*, 1955, [2–3], 610–613).—Quantometry as a method of routine analysis in the aluminium plant of Chippis is described. Indications are given of sparking conditions, quantometer calibration, preparation of calibration samples and average deviation of results. Determinations of amounts of 0·1 to 0·5 per cent. of Si and Fe in the raw metal and 0·01 to 0·001 per cent. of Si, Fe and Cu in the refined metal are accurate to $\pm$ 4 per cent. and $\pm$ 10 per cent., respectively. D. R. GLASSON

2963. **Influence of the molecular structure of oximes on the properties of their compounds with metals.** V. M. Peshkova (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 86–93).—The reactions between various dioximes and metal ions are reviewed; no general conclusions are given. The pH values for pptn., and distribution coeff. and absorption spectra are considered. G. S. SMITH

2964. **Differential determination and detection of oxidants by regulating the pH of the medium.** V. P. Tolstikov (*Zavod. Lab.*, 1955, **21** [2], 140–144).—The differentiation of oxidants, by their behaviour towards KI in relation to the pH of the solution, is studied. With 1 g of KI dissolved in 10 ml of the appropriate buffer solution and 10 ml of a 0·1 *N* solution of the mixture of oxidants, titration with thiosulphate is carried out after a definite interval of time. Determination of iodate, 5 min. after mixing, is accurate at pH 4·0 to 4·5 when an equivalent amount of bromate is present; the error is $\pm$ 2 per cent. with a ten-fold excess of bromate. Iodate in the presence of vanadate can be titrated at pH 4·0 to 4·5, of selenite at pH 3·0 to 4·5 and of arsenate at pH 2·0 to 4·5. Determinations of permanganate can be carried out satisfactorily in the presence of the following ions: bromate at pH 4·0 to 4·5, arsenate at pH 1·5 to 3·5 and molybdate at pH 0·1 to 2·0; in the presence of vanadate the determination is not satisfactory. The possibility of qual. tests is studied by mixing 1 ml of the oxidant solution (0·2 *N*) with 2 ml of buffer solution and 1 ml of 0·6 *N* KI containing 0·2 per cent. of starch, and observing the development of a blue colour. At pH 7·5, after 2 to 3 min., chlorite can be detected in the presence of iodate; at pH 6·5 chlorite reacts instantaneously, whilst nitrite, bromate, selenite, arsenate and antimonate do not react, even on standing. At pH 6·5, after 1 to 2 min., iodate can be detected when accompanied by nitrite, bromate, selenite, arsenate and antimonate. After 1 min., nitrite can be detected in the presence of bromate at pH 5·5, and of selenite, arsenate and antimonate at pH 5·0. Bromate can be detected in the presence of selenite and arsenate at pH 4·0, and selenite in the presence of tellurite, arsenate and antimonate at pH 3·0. G. S. SMITH

2965. **Use of Complexones in chemical analysis. XLV. Contribution to the paper electrophoresis of some metals.** K. Macek and R. Přibil (*Coll. Czech. Chem. Commun.*, 1955, **20** [3], 715–716).—The use in paper electrophoresis of complex-forming reagents, of the EDTA type, has been studied. It often affords better analytical separation of metal ions, and could serve as a rapid and simple method for studying the formation of complexes and their properties, such as charge and pH-stability. [This is a translation into English of a paper originally published in *Chem. Listy*, 1955, **49**, 367.] A. R. ROGERS

2966. **Luminol [3-aminophthalhydrazide] indicator paper for detection of hydrogen peroxide.** A. A. Ponomarenko (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 132–133).—Luminol paper is prepared by shaking a 0·5 per cent. solution of luminol (3-aminophthalhydrazide) in 0·1 *N* NaOH with ashless filter-paper. The paper is then placed for a few min. in a desiccator containing formic acid (to neutralise the alkali) and then dried at 40° C. To detect $H_2O_2$ in a solution, a drop is placed on the prepared paper, then a drop of a catalyst (*e.g.*, 0·1 g of CuCl in 100 ml of 1 per cent. aq. $NH_3$ soln.) and the spot is examined for luminescence. In a dilution of 1:200,000, $H_2O_2$ gives a bright luminescence. Various other possibilities of the use of the paper for luminescent spot tests are suggested. G. S. SMITH

2967. **Flame-spectrophotometric analysis of glasses and ores. I. Lithium, sodium, potassium, rubidium and caesium.** J. P. Williams and P. B. Adams (*J. Amer. Ceram. Soc.*, 1954, **37**, 306–311).—The alkali elements were rapidly determined, without making chemical separations, in a wide range of glass and felspar-ore compositions. Flame-photometer response to Li, Na and K is little affected by the presence of most of the glass constituents in concn. ranges commonly found in commercial glasses. The mean deviation between chemical and flame-photometer analyses for 29 glass and ore samples is $\simeq$ 0·15 per cent. Evaluation of the results for Rb and Cs was not possible since chemical analyses for these elements were not available. CHEM. ABSTR.

2968. **Determination of sodium and potassium in complex cyanide solutions by means of anion-exchange resins.** G. Gabrielson (*Analyst*, 1955, **80**, 479–481).—In the method described by Samuelson (*Svensk Kem. Tid.*, 1945, **57**, 158), Na and K are separated from complex cyanides by passing the solutions through a hydrogen-saturated cation-exchange resin of the sulphonic acid type. Accurate separation was obtained by this method for complex cyanides of the alkali metals with Fe, Co, Cr, Mo and W, but not for complex cyanides of Zn and Ni. In the determination of alkali metals in complex cyanides of Cu and Zn in plating solutions, the soln. was allowed to percolate through a strongly basic anion-exchange resin in the hydroxyl form. In the eluate only alkali metals were present, and these were titrated with 0·1 *N* HCl. Recovery of alkali metals from $K_3Fe(CN)_6$, $K_4Fe(CN)_6.3H_2O$, $Na_2Zn(CN)_4$, $Na_2Cu(CN)_3$ and $K_2Ni(CN)_4.H_2O$ is good, the max. relative error being ± 0·4 per cent.
A. O. Jones

2969. **Determination of potassium in the presence of sodium by means of a flame photometer.** R. Neumann (*Čas. Lék. Čes.*, 1954, **93**, 1229–1231).—If the concn. of Na in the sample is > 1 per cent., the magnitude of the galvanometer deflection becomes practically independent of small variations of concn. A standard curve for K in the sodium flame is not linear and does not run through the origin, but it can be used in the full range of concn. of K. The air required for the operation of the flame photometer can be provided from a low-pressure compressor; the air pressure can be controlled by means of a flow-meter or an open mercury manometer.
Chem. Abstr.

2970. **Sedimetric method for potassium and ammonium determination.** D. Kaplan and J. Schnerb (*Bull. Res. Coun. Israel*, 1955, **4** [4], 397–398).—The method previously described (*Anal. Abstr.*, 1955, **2**, 37) dealt only with the analysis of salts containing chlorides. It has now been adapted for the determination of K in nitrates and sulphates, and of $NH_4^+$. The quantities of liquid centrifuged [with 15 ml of $Al_2(SO_4)_3$ solution, sp. gr. 1·33 at 25° C] are, respectively, $K_2SO_4$, 10 ml ≡ 1 g of sample; $KNO_3$, 5 ml ≡ 1 g of sample; ammonium salts, 2 ml ≡ 0·5 g of sample. Centrifugation was carried out at 1500 r.p.m. for 1 min., and not 3000 r.p.m. for 10 min., as erroneously stated in the earlier paper.
S.C.I. Abstr.

2971. **Potentiometric titration of potassium halides against silver nitrate with the glass electrode.** W. Hubicki (*Ann. Univ. M. Curie-Skłodowska*, 1953, **8** [6], 149–160; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 584).—The pptn. of halides with $AgNO_3$ is studied potentiometrically with a glass electrode. The potentiometric curves for the direct titrations against $AgNO_3$ have maxima at the equivalence points, and the reverse titration curves have corresponding minima; the formation of silver halides is accompanied by adsorption effects. The addition of electrolytes that do not react with $AgNO_3$ sharply reduces the height of the maxima or the depth of the minima. In the presence of Na acetate - acetic acid buffer, the curves show no extreme values. Various alcohols, pyridine and adsorption indicators do not affect the titration results. The straight-line potentiometric graphs for the formation of $Hg(SCN)_3$ and the halides of $Hg^I$ and $Pb^{II}$ indicate the absence of adsorption effects in these reactions.
E. Hayes

2972. **Determination of potassium and sodium in siliceous, argillaceous and phosphatic rocks by the flame photometer.** L. Jenkins (*U.S. Atomic Energy Comm.*, TEI-453, 1954, 17 pp.).—Ignite a 0·5-g sample gently in platinum to remove organic matter. Add 10 ml of 7·5 *N* $HNO_3$, 3 ml of $HClO_4$ and 5 ml of HF. Evaporate to 5 ml on a steam-bath and then to 1 ml on a hot-plate. Cool, add 25 ml of $H_2O$, digest on a steam-bath, transfer to a 100-ml flask and dilute to vol. Read the transmission in a Beckman DU spectrophotometer, with Beckman flame attachment, at 767 mμ for $K_2O$ and at 589 mμ for $Na_2O$, bracketing the unknown soln. with nearest higher and lower standard of $K_2O$ and $Na_2O$, respectively. A correction is applied to the value obtained for $Na_2O$ for the enhancing effect of the $K_2O$ present. No separation is necessary. An accuracy of ± 3 per cent. is claimed.
Chem. Abstr.

2973. **Determination of caesium as caesium bismuth iodide.** V. E. Plyushchev and B. G. Korshunov (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 119–123).—Improvements in the $Cs_3Bi_2I_9$ method (Wells and Foote, *Amer. J. Sci.*, 1897, **3**, 461; Tananaev and Garmash, *Z. anal. Chem.*, 1932, **89**, 256) are described.
G. S. Smith

2974. **The effect of the substrate on two catalytic spot-tests for copper.** R. M. Rush and L. B. Rogers (*Mikrochim. Acta*, 1955, [4], 821–823).—Application of two copper-catalysed spot-tests to 22 grades of filter-paper shows at least a ten-fold variation in sensitivity with the grade of filter-paper, the ash-free grades being generally the most sensitive. The reactions used were the autoxidation of resorcinol and the reduction of *o*-dinitrobenzene by phenylhydrazine.
W. J. Baker

2975. **The colorimetric determination of copper with di-(2-hydroxyethyl)dithiocarbamate.** J. E. Delaney (*Sanitalk*, 1954, **2** [4], 11–14).—The standard method of determining copper colorimetrically with sodium diethyldithiocarbamate has many disadvantages, which the author lists. These disadvantages are overcome to a great extent if di-(2-hydroxyethyl)dithiocarbamate is used as reagent. The addition of 1 ml of pyrophosphate soln. to eliminate interference by iron in concn. up to 20 p.p.m. is preferable to the 5 ml of pyrophosphate originally proposed. Maximum absorption occurs at 435 mμ. Beer's law is obeyed for concn. up to 70 μg of Cu per 100 ml. The method can be adapted to determine Cu in sewage and trade effluents.
Water Pollution Abstr.

2976. **Polarographic determination of copper in cyanide [plating baths].** J. V. Petrocelli and G. Tatoian (*Plating*, 1955, **42** [5], 550–552).—Transfer, by pipette, a 0·25-ml sample of the plating solution into a 50-ml flask, add 2 ml of 0·2 per cent. gelatin solution and dilute to the mark with supporting electrolyte (6·8 *N* $CaCl_2.2H_2O$ and 3·0 *N* HCl). De-aerate with nitrogen, and subject to polarography, reading the current at − 0·25 V and − 0·65 V. The difference between the two readings = diffusion current for Cu.
N. E.

2977. **Polarographic determination of copper, nickel, cobalt, manganese and chromium in titanium alloys.** J. J. Mikula and M. Codell (*Anal. Chem.*, 1955, **27** [5], 729–732).—The following procedures are recommended. *Copper, nickel and cobalt*—The titanium alloy (0·1 g) is dissolved in water containing

48 per cent. HF (15 to 20 drops) and a few drops of $HNO_3$. The soln. is evaporated almost to dryness with 72 per cent. $HClO_4$ (2 ml). The residue is dissolved in conc. HCl (2 ml), washed into a 100-ml calibrated flask with 50 to 75 ml of water and, if Cr is present, 10 per cent. $BaCl_2.2H_2O$ (5 ml) is added. Pyridine ($\simeq$ 13 *M*) (5 ml) and gelatin soln. (1 per cent.) (5 ml) are then added, and the mixture is made up to the mark. After the ppt. has settled, the supernatant liquid is examined polarographically between 0 and − 1·3 V *vs.* the S.C.E. Concn. of $Cu^{++}$, $Ni^{++}$ and $Co^{++}$ are obtained, via calibration curves, from the heights at respective $E_{\frac{1}{2}}$ values of − 0·25, − 0·78 and − 1·06 V, or from diffusion-current data. *Manganese*—The sample (0·1 g) is dissolved as described above and the soln. is treated with saturated aq. $Ba(OH)_2$ at 0° C until a faint ppt. appears. The pH is adjusted to approx. 6·6 with solid $BaCO_3$ (methyl red), then 0·5 per cent. gelatin soln. (2 ml) is added and the soln. is made up to 100 ml. After settling of the ppt., the supernatant liquid is examined polarographically between − 1·3 and − 1·8 V *vs.* the S.C.E., and the $Mn^{++}$ concn. is obtained from diffusion-current data. *Chromium*—The sample (0·1 g) is dissolved in 20 per cent. $H_2SO_4$ (5 ml) and 48 per cent. HF (15 to 20 drops) in the presence of Fe (25 mg). The soln. is heated to fumes of $H_2SO_4$ after addition of $HNO_3$ (2 to 3 drops, if necessary). The soln. is diluted to approx. 100 ml with water and boiled (5 min.), and to the resulting suspension are added 0·25 per cent. aq. $AgNO_3$ soln. (5 ml) and $(NH_4)_2S_2O_8$ (1 g). After being boiled (10 to 15 min.), the soln. is cooled, neutralised with 4 *N* NaOH to ppt. the $Fe^{+++}$, and then treated with 4 *N* NaOH (20 ml) containing 30 per cent. $H_2O_2$ (25 to 30 drops). The mixture is evaporated rapidly to a vol. of 15 to 20 ml, then made up to 50 ml with water in the presence of 0·5 per cent. gelatin (1 ml). The soln. is examined polarographically between − 0·4 and − 1·6 V *vs.* the S.C.E., and the $Cr^{+++}$ concn. is calculated from a calibration curve of diffusion-current data. If a purple colour due to $Mn^{++}$ results after the addition of $S_2O_8^{--}$, the soln. is treated as follows. Conc. HCl (1 ml) is added and, after boiling (10 min.), the suspension is filtered, and the boiling filtrate is neutralised with 4 *N* NaOH. Aq. $NH_3$ (20 ml) and saturated bromine water (20 ml) are added and the soln. is again boiled. After filtration, the boiling filtrate is treated with 4 *N* NaOH (20 ml) containing 30 per cent. $H_2O_2$ (25 to 30 drops) and, after a further filtration, the soln. is boiled to a small vol., made up to 50 ml and examined polarographically as above. On a 0·1-g sample, the limits of applicability are: 0·2 to 5 per cent. of Co, Ni and Cu, in the presence of each other, 1 to 10 per cent. of Mn, and 0·05 to 20 per cent. of Cr. Results are presented for the analysis of 29 synthetic mixtures and 2 titanium alloys. D. A. PANTONY

2978. **Polarographic determination of traces of copper, nickel, cobalt, zinc and cadmium in rocks, using rubeanic acid and 1-nitroso-2-naphthol.** L. E. Smythe and B. M. Gatehouse (*Anal. Chem.*, 1955, **27** [6], 901–903).—Rubeanic acid may be used for the determination of Cu, Ni and Co and other metals in the presence of Fe, Al and other interfering ions. The rubeanates of Cu, Ni, Co, Zn and Cd are stable and insoluble and are selectively and quant. pptd. under carefully controlled conditions. Cobalt is separated as the nitrosonaphthoxide and estimation of the elements is performed polarographically. The method has been applied to a number of rock samples, and its accuracy compares favourably with that of other methods, although it depends on the gravimetric procedures adopted before taking the polarogram. Limitations are offset by a reduction in the final volume of the sample solution. A. J. MEE

2979. **Determination of copper in copper - nickel alloys.** A. Wogrinz and G. Wyk (*Prakt. Chem.*, 1955, **6** [4], 93).—Turnings of the alloy are dissolved in warm conc. HBr (15 to 30 ml) in a Kjeldahl flask. When evolution of bromine vapour ceases, aq. $H_2O_2$ is added by pipette to the dark-brown solution, which is warmed to expel excess of Br, the solution is diluted with water (30 ml) and boiled. It is then washed into the titration flask and acidified with acetic acid; Cu in the solution is determined iodimetrically. A. R. PEARSON

2980. **Solubility products of copper, nickel and cobalt rubeanates.** D. P. Malyuga (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 107–110).—The solubilities of the rubeanates of Cu, Ni and Co in pure water, 0·01 *M* aq. $NH_3$ soln., 0·001 *M* HCl, and a solution containing 0·1 *M* $NH_4Cl$, 0·1 *M* citric acid and 0·001 *M* NaOH are, respectively, Cu, $5{\cdot}8 \times 10^{-8}$, $7{\cdot}7 \times 10^{-7}$, $3{\cdot}0 \times 10^{-7}$, and $6{\cdot}8 \times 10^{-8}$; Ni, $7{\cdot}2 \times 10^{-8}$, $7{\cdot}6 \times 10^{-7}$, $1{\cdot}1 \times 10^{-6}$, and $7{\cdot}5 \times 10^{-8}$; Co, $7{\cdot}4 \times 10^{-8}$, $9{\cdot}0 \times 10^{-7}$, $6{\cdot}7 \times 10^{-7}$, and $5{\cdot}4 \times 10^{-8}$ (moles per litre, at 18° C). The solubility products are: Cu, $7{\cdot}67 \times 10^{-16}$; Ni, $1{\cdot}1 \times 10^{-15}$; Co, $1{\cdot}2 \times 10^{-15}$. G. S. SMITH

2981. **Use of EDTA (disodium salt) in the analysis of beryllium bronze.** V. G. Goryushina (*Zavod. Lab.*, 1955, **21** [2], 148–149).—EDTA (disodium salt) (**I**) is used for determining Be in Cu - Be bronze by the gravimetric phosphate method. Beryllium is separated from most of the Cu either by electrolysis, followed by the addition of a small amount of **I** to the spent electrolyte to combine with traces of Cu, or by direct pptn. of phosphate after addition of sufficient **I** to combine with all the Cu. *Procedure*—The bronze (0·5 g) is dissolved in 10 ml of $HNO_3$ (1 + 1) in the cold and the solution is boiled to remove oxides of nitrogen. For the electrolytic separation, the solution is diluted to 150 ml, 5 g of $NH_4NO_3$ and 5 ml of $H_2SO_4$ (1 + 1) are added, and most of the Cu is removed at 2 to 3 amp. The electrolyte is then evaporated to 100 ml, and 5 ml of a 15 per cent. solution of **I** (prepared by mixing 15 g with a small amount of water, adding aq. $NH_3$ soln. to dissolve the undissolved matter, diluting to between 70 and 80 ml with water, filtering, adding HCl to give a pink colour with methyl red, then ammonia to make alkaline, and water to 100 ml), 3 ml of 2 *M* $(NH_4)_2HPO_4$, sufficient aq. $NH_3$ (1 + 1) solution to give a permanent cloudiness and 20 ml of 15 per cent. ammonium acetate solution are added. The solution is boiled for 2 to 3 min. and then kept hot to render the ppt. crystalline. The ppt. is filtered off, washed with 1 per cent. $NH_4NO_3$ solution (neutralised to methyl red) and finally ignited at 800° to 850° C. For the direct method, the solution, diluted to 80 to 100 ml, is treated with 20 ml of a solution of **I**, 6 ml of ammonium phosphate solution, aq. $NH_3$ soln. and ammonium acetate, as described above. The crystalline ppt. is filtered off, washed, redissolved in hot HCl (1 + 4) and repptd., 5 ml of **I** solution, 2 ml of $(NH_4)_2HPO_4$ solution, aq. $NH_3$ soln. and ammonium acetate being used as before. The error with either method does not exceed $\pm$ 0·02 per cent. on a sample containing 2·12 per cent. of Be. G. S. SMITH

2982. **The determination of small amounts of magnesium with Eriochrome black.** J. K. R. Gasser (*Analyst*, 1955, **80**, 482–484).—In the method described, the sum of the Ca and Mg present is determined by titration with ethylenediaminetetra-acetic acid (**I**), and the Mg absorptiometrically with Eriochrome black T, a correction factor for the Ca present then being applied. A. O. JONES

2983. **Photometric determination of minute amounts of magnesium in zinc plate for dry batteries.** M. Suzuki (*Japan Analyst*, 1954, **3** [2], 93–96).—In the pptn. of Mg oxinate in an ammoniacal soln., Zn, Cd and Hg can be masked by the addition of a sufficient amount of KCN. The separation of Pb is achieved by pptg. Mg and Fe (added) with NaOH. Traces of Pb adsorbed on the hydroxide ppt. can be removed by co-pptg. with $Fe(OH)_3$ on treatment with aq. $NH_3$ soln. Magnesium oxinate is dissolved in HCl and the amount of oxine is determined colorimetrically with sulphanilic acid and $NaNO_2$. *Procedure*—The sample (0·5 g) is dissolved in 6 *N* HCl, and 1 ml of 1 per cent. $FeCl_3$ soln. is added; NaOH soln. (50 per cent.) is then added until the pptd. $Zn(OH)_2$ dissolves. The residual ppt. of $Mg(OH)_2$ and $Fe(OH)_3$ is filtered off, dissolved in dil. HCl (1 + 2), made alkaline with aq. $NH_3$ soln., boiled with 10 per cent. $(NH_4)_2S_2O_8$ soln. (2 ml) (to ppt. $MnO_2$) and filtered. The filtrate is made acid with HCl and boiled to decompose persulphate. Tartaric acid (20 per cent.) (1 ml), aq. $NH_3$ solution (1 + 1) and KCN (40 per cent.) (1 ml) are added and Mg is pptd. as oxinate, which is dissolved in 0·2 *N* HCl. A portion of the acidic soln. is treated with sulphanilic acid (4·5 g per 100 ml of 3 per cent. acetic acid) (1 ml) and $NaNO_2$ (0·5 per cent.) (1 ml). The extinction is proportional to the concn. for up to 500 $\mu$g of Mg per 100 ml. K. SAITO

2984. **Colorimetric determination of micro quantities of calcium.** T. T. Gorsuch and A. M. Posner (*Nature*, 1955, **176**, 268–269).—Calcium in the range 0 to 8 $\mu$g per 10 ml can be determined colorimetrically with murexide (ammonium purpurate) at pH 11·0, the colours showing no appreciable change in 15 min. A known volume of calcium solution is added to 1 ml of 0·03 *N* KOH and the solution is made up to 5 ml with water. Murexide solution (5 ml) (prepared fresh daily and containing 20 mg per litre) is added immediately before determining the red colour in a Hilger Spekker absorptiometer. A graph shows the linear relationship between the colour and concn. of Ca. Ammonium ions and those of Na, K, $Al^{III}$ and $Mn^{II}$, when present in a 20-fold excess (molecular basis) over the $Ca^{++}$, and $Ba^{++}$ in a 10-fold excess do not interfere with the colour due to the $Ca^{++}$. When present in amounts comparable to the $Ca^{++}$, Cu, $Zn^{++}$, $Cd^{++}$, $Hg^{++}$, $Ag^{+}$ and $Co^{++}$ interfere considerably, $Sr^{++}$ and $Mg^{++}$ give results 10 per cent. too high, and $Fe^{++}$ and $Fe^{+++}$ give a result 4 to 5 per cent. too low. The use of KCN (≃ 1 g per litre) in the KOH soln. completely eliminates interference from Cu, $Hg^{++}$, $Ag^{+}$, $Co^{++}$ and $Cd^{++}$. The effects due to $Zn^{++}$, $Fe^{++}$, $Fe^{+++}$, $Sr^{++}$ and $Mg^{++}$ are largely unaffected by KCN. O. M. WHITTON

2985. **A rapid method of determining calcium in magnesite.** H. Flaschka and H. Jakobljevich (*Radex Rundschau*, 1954, 83–86).—Dissolve 2 g of magnesite in HCl with a few drops of $HNO_3$. Filter, and dilute the filtrate and washings to 500 ml. Mix and take 200 ml of the soln. for the determination of sesquioxides. Neutralise the remaining 300 ml with NaOH; add 3 to 5 ml of aq. triethanolamine soln. (50 per cent.) and 25 ml of 0·05 *M* EDTA (disodium salt). Dilute to about 450 ml; then add, with shaking, about 15 ml of 4 *N* NaOH, dilute to 500 ml and shake thoroughly. Let stand for 30 to 60 min., withdraw 200 ml of the clear liquid, add 5 ml of 4 *N* NaOH and sufficient murexide indicator to produce a blue - violet colour. Titrate at once with 0·05 *N* $CaCl_2$ soln. to a sudden colour change to red - violet. CHEM. ABSTR.

2986. **Automatic photometric titrations of calcium and magnesium in carbonate rocks.** L. Shapiro and W. W. Brannock (*Anal. Chem.*, 1955, **27** [5], 725–728).—The carbonate rock is decomposed by standard methods, and a 10-ml aliquot of the soln., containing 20 mg of sample, is diluted with 200 ml of water, and treated with 15 per cent. aq. NaOH (10 ml) and 0·2 per cent. aq. murexide indicator (1 ml). A 10 to 20-ml portion is removed from the soln. and the remainder is titrated visually with an accurately measured vol. of standard 0·175 per cent. EDTA (disodium salt) (**I**). The removed portion of soln. is replaced, and the titration is continued automatically (photo-electric recorder coupled with the titrimeter) with 0·1 per cent. **I**. Allowance having been made for a blank, the total titre represents the concn. of $Ca^{++}$; Mg is determined similarly, after removal of insol. hydrated oxides with aq. $NH_3$, and of $Ca^{++}$ with $WO_4''$, Eriochrome black T being used as indicator. Results are compared with those of standard procedures on 12 samples. D. A. PANTONY

2987. **A note on the determination of calcium oxide or hydroxide in lime and silicate products.** M. R. Verma, V. M. Bhuchar, K. J. Therattil and S. S. Sharma (*J. Sci. Ind. Res., B, India*, 1955, **14** [4], 192–193).—A volumetric method in which $Ca^{++}$ present in solutions are determined directly has been applied to the determination of "available lime" in various commercial limes. The titrating agent is EDTA (disodium salt) and Eriochrome black T the indicator. *Procedure*—A known weight of the material to be analysed was shaken with 500 ml of neutral 2 per cent. sucrose solution in a closed vessel for 2 hr. The solution was then filtered and aliquots were titrated against (*i*) standard solution of EDTA (disodium salt) and (*ii*) standard acid, with phenolphthalein as indicator. Available lime is calculated from the lime content obtained in the sucrose extract, (*a*) directly by the EDTA method and (*b*) from titrable hydroxide by the alkalimetric method. The values were consistently higher than those obtained by the usual alkalimetric method and it is suggested that this method should not be continued as the basis for "available lime" determination without further critical examination. G. C. JONES

2988. **Flame-photometric determination of strontium in Portland cement.** J. J. Diamond (*Anal. Chem.*, 1955, **27** [6], 913–915).—An accurate method for the determination of Sr in the presence of 150 to 3000 times as much Ca is described; the technique of flame photometry, which requires no previous chemical separation, is used. The possible interference of Li is studied, and is found to be negligible. Samples are prepared so that Na and K as well as Sr can be determined. A. J. MEE

2989. **Control of the thickness of passivated zinc deposits.** M. E. Gol'dshtein (*Zavod. Lab.*, 1955, **21** [2], 204).—The jet and drop methods of determining the thickness of zinc deposits give high and

variable results when the Zn is passivated. Correct results are obtained by the magnetic method. The passivation does not contribute to the thickness.
G. S. SMITH

2990. **Determination of cadmium in the presence of copper by the method of derivative polarographic curves.** K. S. Pakhomova and A. S. Krivyakova (*Zavod. Lab.*, 1955, **21** [2], 144–147).—The method of Leveque (*J. Chim. Phys.*, 1949, **40**, 9) is found to be satisfactory for determining Cd and Cu when present together. G. S. SMITH

2991. **Simultaneous polarographic determination of cadmium and zinc in alkaline cyanide solutions.** T. A. Downey (*Plating*, 1955, **42** [3], 267–270).—Cadmium and zinc are determined polarographically in a supporting electrolyte that is 0·36 *N* in $NH_4Cl$, 0·6 *N* in aq. $NH_3$ and 0·01 per cent. in gelatin. Cyanides are removed by heating 1 ml of the soln. with 1 ml of conc. HCl. Standards are run with each series of sample solutions. The common metallic impurities found in plating baths do not interfere. N. E.

2992. **Quantitative determination of mercuric ions based on the catalytic oxidation of ferrocyanide.** T. Pinter and H. Dresner (*Mikrochim. Acta*, 1955, [4], 803–805).—A quant. procedure for determining $Hg^{++}$ in concn. from 5 to 50 μg per ml is based on the part-oxidation of $K_4Fe(CN)_6$ to Prussian blue through the catalytic action of $Hg^{++}$. The intensity of the blue colour produced is proportional to the concn. of $Hg^{++}$ and is measured at 660 mμ in a photo-electric colorimeter. The error is about ± 4 per cent. W. J. BAKER

2993. **Methods of analysis for boric acid. I. Visual and potentiometric titration of boric acid.** J. J. Sciarra and J. A. Zapotocky (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [6], 370–372).—A comparison of the effectiveness of replacing glycerol in visual and potentiometric assays of boric acid shows that mannitol, invert sugar, fructose, propane-1:2-diol and ethanediol can replace glycerol in the U.S.P. assay; ethanediol gives the best results. Maltose, lactose, starch, dextrin, and Tween 20 and 80 are ineffective. A potentiometric method of titration is described. G. R. WHALLEY

2994. **Methods of analysis for boric acid. II. Polarimetric analysis of boric acid.** J. J. Sciarra and J. A. Zapotocky (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [6], 373–375).—A polarimetric method for the determination of boric acid is described in which the change in optical activity obtained when a soln. containing 1 per cent. or less of boric acid is mixed with 10 per cent. *d*-tartaric acid soln. at room temp. is used. The construction of a standard graph permits the rapid determination of boric acid, with an accuracy within the limits of the U.S.P. assay, that is, a visual titration method. Boric acid does not form optically active complexes with amino acids, or citric and lactic acids, and is little affected by arabinose, D-mannose, D-xylose or fructose. G. R. WHALLEY

2995. **Method of determining boric acid by saturation.** L. A. Maĭ and I. I. Yurdanov (*Zavod. Lab.*, 1955, **21** [2], 162–163).—In certain instances the separation, *e.g.*, by distillation, of $H_3BO_3$ from heavy-metal salts and tetraborates before its determination can be avoided by means of a saturation method. *Procedure*—To the solution (100 to 250 ml) are added 5 to 10 g of finely powdered $H_3BO_3$ and 0·5 to 1 g of a detergent. The soln. is shaken for 0·5 to 1 hr., then maintained with an excess of $H_3BO_3$ at a const. temp. (± 0·5° C) for 1 hr., filtered through a glass crucible, dried at 40° to 50° C, then washed with 10 to 15 ml of dry acetone; the $H_3BO_3$ is dried at 40° to 50°C. The concn. of $H_3BO_3$ in the original solution is calculated from the formula:

$H_3BO_3$ (grams per litre) $= S - 1000\ (m - w)/V$,

where $V$ is the vol. (ml) of the solution taken, $m$ is the weight (g) of added $H_3BO_3$, $w$ is the weight (g) of the residual $H_3BO_3$, and $S$ is the solubility of $H_3BO_3$ in water at the temp. used, *e.g.*, 50·4 g per litre at 20° C. The use of a detergent can be avoided by heating to between 50° and 60° C, cooling, keeping for 3 to 4 hr. at the chosen temp. and seeding with crystals of $H_3BO_3$. With 1 *N* solutions, the method is accurate to $\simeq$ 5 per cent., if alkali salts and acids are absent. G. S. SMITH

2996. **Quantitative determination of fluoroboric acid in the presence of free boric acid, by the use of cetyltrimethylammonium chloride [cetrimonium chloride].** H.-J. Schaack and W. Wagner (*Z. anal. Chem.*, 1955, **146** [5], 326–338).—Cetrimonium chloride (**I**) is found to be a suitable reagent for the quant. determination of fluoroboric acid in the presence of hydrofluoric and boric acids. In former methods nitron was used to ppt. nitron fluoroborate (**II**); a correction was necessary owing to the high solubility of **II**. By the addition of an excess of a solution of **I**, $HBF_4$ separates quant. as a white crystalline precipitate ($C_{19}H_{42}N.BF_4$). This compound has a solubility < 10 per cent. of that of **II**. The solution is neutralised with alkali and the ppt. is separated by filtration. The excess of **I** is pptd. with an excess of a standard solution of $K_4Fe(CN)_6$ in $H_2SO_4$; the excess of $K_4Fe(CN)_6$ is titrated with standard $KMnO_4$ soln.; hence the original amount of fluoroboric acid can be calculated. A. J. MEE

2997. **Fluorimetric determination of aluminium and gallium in mixtures of their oxinates.** J. W. Collat and L. B. Rogers (*Anal. Chem.*, 1955, **27** [6], 961–965).—Aluminium and gallium oxinates have essentially identical fluorescence spectra in chloroform. Both emit a strong yellow-green fluorescence in chloroform when irradiated with the 3650 A mercury line. The method described is based on the difference in their sensitivities to different wavelengths of exciting radiation; standard spectrophotometers were modified to provide monochromatic exciting radiation, and to permit the determination of the individual components. The precision and accuracy of the method decline at high concn. of Al and Ga. A. J. MEE

2998. **Photometric determination of aluminium in phosphate materials with ferron.** M. Delevaux, R. Smith and F. S. Grimaldi (*U.S. Atomic Energy Comm.*, TEI-450, 1954, 19 pp.).—Ignite a 0·3333-g sample in platinum to remove organic matter. Add 5 ml of 7·5 *N* $HNO_3$, 5 ml of HF and 5 ml of $HClO_4$. Evaporate on a steam-bath and then fume on a hot-plate to 1 ml. Add 62 ml of 6 *N* HCl, digest, filter into a 200-ml flask and dilute to vol. Transfer 3 ml by pipette into a 15-ml glass-stoppered centrifuge tube, followed by 2 ml of aq. cupferron soln. (3 per cent.), and extract with 10 ml of $CHCl_3$. Centrifuge for 10 min. Transfer by pipette 1 ml of the aq. layer into a 30-ml beaker. Add 2 ml of 7·5 *N* $HNO_3$ and evaporate to dryness.

Add 1 ml more of the $HNO_3$ and 2·5 ml of $HClO_4$ and evaporate on a steam-bath and then on a hot-plate until no fumes of $HClO_4$ are evident, to remove traces of cupferron. With a burner heat the beaker not above 300° C to remove the last traces of $HClO_4$. Add 2 ml of HCl and digest on a steam-bath for 10 min. to convert any pyrophosphate into orthophosphate. Evaporate to dryness on a steam-bath, add 5 ml of 1 per cent. HCl, digest and transfer to a 25-ml flask. Add, by pipette, 5 ml of aq. ferron soln. (0·16 per cent.) and 5 ml of buffer soln. (412 g of $NH_4$ acetate and 109 ml of glacial acetic acid per litre) into the flask and dilute to the mark. Read the absorbancy of the soln. at 370 mμ. Use as a blank a soln. containing the same amounts of HCl and buffer. The pH of the final soln. must be between 5·0 and 5·6 and the amount of $P_2O_5$ present must be $< 400$ μg. Fluorine must be absent. An accuracy of ± 3 per cent. is claimed on samples containing up to 30 per cent. of $Al_2O_3$.

CHEM. ABSTR.

2999. **Detection of gallium with rhodamine B.** Hiroshi Onishi (*Anal. Chem.*, 1955, **27** [5], 832).—Gallium is specifically detected by mixing a soln. (2 ml), made 6 *M* with respect to HCl, with rhodamine B soln. (0·5 per cent. in 6 *M* HCl) (0·4 ml) and extracting the complex with benzene (2 ml). A pink to red colour and an orange - yellow fluorescence in u.v. light in the org. phase are characteristic of Ga$^{\cdots}$. Interference due to Sb$^{\cdots}$, Fe$^{\cdots}$, Au$^{III}$, Tl$^{\cdots}$ and W$^{VI}$ is eliminated by the addition of 20 per cent. $TiCl_3$ soln. (0·5 ml) and centrifuging before the test is applied; other non-interfering elements are listed. The limit of detection is $\simeq$ 0·01 μg of Ga$^{\cdots}$.

D. A. PANTONY

3000. **Quantitative spectrographic analysis of rare-earth elements.** V. A. Fassel, B. Quinney, L. C. Krotz and C. F. Lentz (*Anal. Chem.*, 1955, **27** [6], 1010–1014).—Emission spectrometric methods are described for the quantitative determination of rare earths commonly associated with purified Dy, Ho and Er, namely, Ho, Er, Y and Tb in Dy; Y, Dy and Er in Ho; and Y, Dy, Ho, Tm and Yb in Er. Direct-current carbon-arc excitation of rare-earth oxide - graphite mixtures is employed, and the methods cover concentration ranges up to 1 per cent. A high degree of internal standardisation is attained in rare-earth systems by this method, which makes use of the unique similarity in excitation behaviour among many of the rare earths. It was observed that the Ho 3456·00 A line, used in the determination of Ho in Dy and Er, undergoes strong self-reversal.

A. J. MEE

3001. **Determination of carbon in sodium - potassium alloy.** K. G. Stoffer and J. H. Phillips (*Anal. Chem.*, 1955, **27** [5], 773–776).—Full details are given for the extraction (under N) of 100-mg samples of liquid Na - K alloys from a heat-exchanger system. The sample is burnt in O and the resulting $CO_2$ is absorbed and weighed as in the normal method for the micro-determination of C. The precision is stated to be the same as that of micro-determinations of C.

D. A. PANTONY

3002. **Colorimetric determination of cyanides with the benzidine - pyridine reagent.** W. Christ (*Wasserwirtsch.-Wassertech.*, 1954, **4**, 369–371).—The determination of CN′ in sewage and similar samples is discussed. The Liebig titration of CN′ with $AgNO_3$ gives good results when the concn. of CN′ is large, but the colorimetric determination with the benzidine - pyridine reagent (*cf. Chem. Abstr.*, 1945, **39**, 40; 1946, **40**, 1426; 1951, **45**, 10443) is more satisfactory for low concn. Directions are given for using the method with the Zeiss - Pulfrich photometer and the Lange colorimeter.

CHEM. ABSTR.

3003. **Oxidation of thiocyanate by alkaline ferricyanide.** B. Suseela (*Z. anal. Chem.*, 1955, **145** [3], 175–178).—Oxidation of KSCN by alkaline $K_3Fe(CN)_6$ in the presence of osmic acid proceeds at a measurable rate at ordinary temp., but is accelerated on refluxing the system for a short time on a water bath. The stoicheiometry of the redox process suggests the formation of cyanate and sulphate as the products of oxidation. The quantity of thiocyanate is calculated by estimating the ferrocyanide formed and the ferricyanide consumed in terms of $Ce(SO_4)_2$ and $Na_2S_2O_3$, respectively.

P. HAAS

3004. **Silicate analysis in an alternating-current arc.** F. Rost (*Mikrochim. Acta*, 1955, [2–3], 236–243).—Various kinds of glow obtained in continuous carbon arcs are compared and an explanation, with respect to physical conditions, of the "double electrode a.c. arc" between two electrodes filled with material is attempted. It is applied to the analysis of accessory elements in magnesium silicates; Fe, Al and Ca (and Si) are determined in samples of alkali-free magnesium silicate and boiler-scale with accuracies of ± 5 per cent., with Ba acetate as diluting reference substance.

D. R. GLASSON

3005. **Colorimetric analysis in the series of heteropolyacids [of silicon, phosphorus, etc.].** M. Jean (*Chim. Anal.*, 1955, **37** [4], 125–135; [5], 163–172).—Based on a review of the literature (337 references), the probable formation and stability of molybdosilicic, -phosphoric, -arsenic and -germanic acids during analytical procedures are discussed extensively, with special reference to the influence of variables, *e.g.*, pH, time, temp. and molybdate concn., on the stability of the particular acid(s) formed, and on the development and stability of the coloration. Optimum conditions are examined for (*i*) the photometric determination of Si as the yellow molybdosilicic complex at pH $\gtrsim$ 1·5, and (*ii*) the colorimetric determination of Si, P, As or Ge as the respective molybdenum blue complexes, formed, usually at very low pH, by reduction of the corresponding heteropolyacid with $SnCl_2$, $FeSO_4$, hydrazine, etc. The action of oxalic acid, tartaric acid, HF, etc., on $MoO_3''''$ is examined in connection with their use in the selective determination of either Si (by sequestering P and As) or P or As when these are present together. Methods of extracting selectively the heteromolybdic acids from aq. soln. with organic solvents (ethyl acetate, *n*-butanol, *iso*butanol, etc.) are reviewed, and various procedures for the colorimetric determination of As, P, Si and Ge as the blue complexes are summarised. In general, Si is determined by forming the molybdosilicic acid at a pH of approx. 1·5, and increasing the acidity to $\simeq 2N$ before adding the reducing agent (preferably oxalic or tartaric acid); for P, the reducing agent and the molybdate soln. are added simultaneously to the soln. of $\simeq N$ acidity, the reduction being effected at 80° to 90° C; for As, the absorption measurements are made at 840 mμ (Zr, W and Nb interfere); for Ge, Beer's law is valid only at a concn. of 1·5 μg of Ge per litre. In the presence of Si or P, the As or Ge should be separated by distillation as trichloride. The yellow vanadium

complexes of molybdo- and tungsto-phosphoric acids are discussed in relation to the colorimetric determination of P or V (in steel) as the molybdovanadophosphate, of V or W (in steel) as the tungstovanadophosphate, or of As (in pigments) as the molybdovanado-arsenate complexes, respectively. Preferred procedures and the limits of sensitivity are indicated for each method. W. J. BAKER

3006. **Photometric determination of germanium after its paper-chromatographic separation.** I.-M. Ladenbauer and O. Slama (*Mikrochim. Acta*, 1955, [4], 903–910).—The quant. paper-chromatographic procedure described for the separation of Ge from soln. of minerals, dusts, etc., is based on the difference between the $R_F$ value of Ge and that of most other associated elements when a mixture of *n*-butanol and 10 per cent. $HNO_3$ is used as solvent. The Ge is eluted with $H_2O$ in an appropriate device (illustrated) and is then determined photo-colorimetrically with phenylfluorone (2:3:7-trihydroxy-9-phenyl*iso*xanth-6-one). The method cannot be used for minerals containing Bi because $Bi_2S_3$ is partly sol. in aq. $NH_3$, resulting in incomplete separation from Ge. A mean value of 0·034 per cent. was obtained for zinc blende containing 0·037 per cent. of Ge (determined by radioactive measurement). W. J. BAKER

3007. **Rapid determination of tin, antimony and copper in lead bearings.** H. Wiedmann (*Z. Metallkunde*, 1954, **45** [11], 658–661).—To determine Sn, dissolve 1 g of filings in 20 ml of conc. $H_2SO_4$, cool, add 20 ml of $H_2O$ and 60 ml of conc. HCl and shake until the soln. is clear. Add 25 ml of aq. $HgCl_2$ soln. (4 per cent.) and 10 ml of aq. $H_3PO_2$ (40 per cent.), boil for 4 to 5 min. and cool in a stream of $CO_2$. Add some solid $CaCO_3$, 15 ml of aq. KI (10 per cent.), 10 ml of aq. $Al(SCN)_3$ (50 per cent.) and starch soln., and titrate with iodine. To determine Sb, dissolve 1 g of filings in 20 ml of conc. $H_2SO_4$, cool, add 30 ml of cold and 200 ml of hot $H_2O$, add 30 ml of conc. HCl and titrate with $KBrO_3$. To determine Cu, dissolve 1 g of filings in 20 ml of aq. tartaric acid (40 per cent.) and 10 ml of conc. $HNO_3$, boil off fumes of $NO_2$, add 30 ml of conc. aq. $NH_3$ while shaking, make up to 100 ml and determine the colour in a colorimeter with a 570-m$\mu$ filter. Each determination requires 12 to 15 min. and gives very accurate results. CHEM. ABSTR.

3008. **Polarographic determination of lead in beryllium.** R. W. Bane (*Anal. Chem.*, 1955, **27** [6], 1022–1024).—A method of determining Pb directly in the presence of large amounts of Be is described. A solution of Be in HCl acts as the supporting electrolyte. No chemical or electrochemical separations are necessary, and it is suggested that the procedure is suitable for routine analyses, and also for the simultaneous determination of Pb, Cd and Zn in Be. A. J. MEE

3009. **Spectrographic determination of lead in oxygen-free, high-conductivity copper.** S. B. Deal (*Anal. Chem.*, 1955, **27** [5], 753–755).—Lead (0·0005 to 0·005 per cent.) is determined spectrographically in 5-mg specimens of Cu by a standard method (a.c. arc). Intensities are compared with those of standards, using the log intensity ratios of Pb 2833·1 A to Cu 2858·7 A plotted against log concn. of lead. Results are presented for several samples, and are compared with those from a standard dithizone procedure. D. A. PANTONY

3010. **Determination of lead in alloys as phosphate.** W. Hubicki, B. Frank, C. Dziewałtowski and K. Sykut (*Ann. Univ. M. Curie-Skłodowska*, 1953, **8** [6], 177–184; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 622).—The method of Hubicki *et al.* (*Ann. Univ. M. Curie-Skłodowska*, 1950, 53), is applied to the analysis of Pb - Sn alloys. A sample of alloy (0·7 g) is dissolved by heat in 25 ml of conc. $HNO_3$ and the Sn is separated as $\beta$-stannic acid. The filtrate is evaporated to dryness and the residue is dissolved in 100 to 150 ml of cold water; 0·5 ml of conc. $HNO_3$ and 4 ml of $H_3PO_4$ (sp. gr. 1·25) are added and the pH is adjusted to 4 by adding aq. $NH_3$ soln. The finely crystalline ppt. of $PbHPO_4$ is collected, washed, and dried to constant wt. at 200° C. The method is not applicable to Pb - Sb alloys; the ppt. of $Sb_2O_5$ absorbs some Pb and the soln. of $Pb(NO_3)_2$ is not free from Sb. E. HAYES

3011. **Use of Complexones in chemical analysis. XLIV. Iodimetric determination of the higher oxides of lead and manganese.** R. Přibil and J. Čihalík (*Coll. Czech. Chem. Commun.*, 1955, **20** [3], 562–565).—A simple method is described for the iodimetric determination of $PbO_2$ and $MnO_2$. It is based on their reduction with KI in the presence of EDTA (disodium salt) (**I**), which prevents the formation of insoluble products, and binds iron and copper as stable complexes. *Procedure*—To determine $PbO_2$, dissolve the finely ground sample (0·2 g) by stirring it with a soln. of KI (2 g) in 0·1 *M* **I** (10 ml) and 5 per cent. acetic acid (10 ml). Dilute the soln. with water and titrate with 0·1 *M* $Na_2S_2O_3$, with starch as indicator, in the usual way. To determine $MnO_2$, dissolve the sample (50 mg) in a soln. of KI (0·5 g) and sodium acetate (0·5 g) in 0·1 *M* **I** (10 ml) and 5 per cent. acetic acid (10 ml); dilute the soln. and titrate as before. [This is a translation into English of a paper originally published in *Chem. Listy*, 1955, **49**, 51.] A. R. ROGERS

3012. **Catalytic micro-method for identification of titanium (IV).** P. Szarvas and G. Almássy (*Magyar Tud., Akad. Kém. Tud. Oszt. Kozl.*, 1953, **3**, 409–411).—The reduction of sodium alizarin-3-sulphonate with nascent H is markedly catalysed by $Ti^{IV}$ even in small amounts, and the presence of $> 0·5$ $\mu$g of $Ti^{IV}$ results in a green soln. For example, if 2 ml of a test soln. are mixed with 1 ml of HCl (1 + 1), 1 ml of saturated ammonium oxalate soln., 0·5 ml of ethanol, 3 drops of a 0·5 per cent. soln. of Na alizarinsulphonate and a small amount of Zn, the soln. becomes green immediately when the concn. of $Ti^{IV}$ is high, and in 5 to 10 min. when the concn. of $Ti^{IV}$ is low. The limit of identification is 0·5 $\mu$g of $Ti^{IV}$, and of concn. is 1:4,000,000. The following ions do not interfere, even at concn. $>$ 3000 times that of the $Ti^{IV}$: $Fe^{++}$, $Fe^{+++}$, Zn, Al, $Mn^{++}$, $Cu^{++}$, $As^{+++}$, $As^{+++++}$, $Sb^{+++}$, $Sb^{+++++}$, $Sn^{++}$, $Sn^{++++}$, $Co^{++}$, $Ni^{++}$, $Cd^{++}$, $Bi^{+++}$, $Pt^{++++}$, Ca, Sr, Ba, Mg, $Cl'$, $Br'$, $I'$, $SO_4''$, $PO_4'''$, $ClO_3'$, $SO_3''$, $IO_3'$, $SCN'$, $NO_3'$, $NO_2'$, $BO_3'''$ and acetate. If the concn. of $Fe^{+++}$ is high (8,000 to 10,000 times that of $Ti^{++++}$), reduction is effected with Zn in HCl before carrying out the test described above. In general, the only interfering ions are those of $Mo^{VI}$, $W^{VI}$, $V^{V}$ and $Cr^{III}$. CHEM. ABSTR.

3013. **Salicylhydroxamic acid as a colorimetric reagent for titanium.** J. Xavier, A. K. Chakraburtty and P. Ray (*Science and Culture*, 1954, **20**, 146).—Salicylhydroxamic acid is a colorimetric reagent for estimating U, V and Mo (Bhadwic and

Ray, *Science and Culture*, 1952, **18**, 97). It gives a deep-yellow ppt. with Ti in dil. acid soln. The pptn. of Ti is quant. between pH 2·5 and 6·0. The ppt. dissolves in conc. $H_2SO_4$ giving a deep-yellow colour that can be extracted with amyl alcohol and examined colorimetrically at 300 mμ. The max. colour intensity is developed in the presence of 6 *N* to 11 *N* $H_2SO_4$. A 2 per cent. ethanolic soln. of the reagent is used. For each estimation (up to 10 μg of Ti, final vol. 50 ml), 8 ml of the reagent soln. are required to produce the max. absorption. Beer's law is valid for 0·1 to 10 μg of Ti. The colour remains unchanged for 24 hr. Determinations can be made at 18° to 35° C without any change in the optical density of the soln. Interference occurs with Fe, V, $PO_4'''$, $CrO_4''$ and $WO_4''$.

CHEM. ABSTR.

3014. **Colorimetric determination of titanium (IV) with phosphite separation.** G. Almássy and P. Szarvas (*Magyar Tud., Akad. Kém. Tud. Oszt. Kozl.*, 1953, **3**, 413–418).—The colorimetric determination of Ti by means of $H_2O_2$ is modified to eliminate interfering ions such as those of $Fe^{II}$, Ni, Co, Cu, Mn, Cr, Zn, Mg and Al. Separation of Ti from these ions is effected by pptn. in HCl (pH < 1) as $Ti_3(PO_3)_4$ and solution in HCl + $H_2O_2$ for photometric measurement. Before pptn., $Fe^{\cdots}$ are reduced with KI and the I is decolorised with $Na_2S_2O_3$. If Sn is present, it is separated with an excess of NaOH and the ppt. containing Ti is dissolved in dil. HCl. *Procedure*—Place 10 ml of HCl soln. (pH > zero) containing 2 to 20 mg of $TiO_2$ in a 20 to 25-ml centrifuge tube and add 2 ml of $H_3PO_3$ soln. (**I**) (prepared freshly from 90 ml of $H_2O$ and 10 ml of $PCl_3$). Stir the mixture and set aside for 20 min. Centrifuge and discard the supernatant liquid. Centrifuge the ppt. twice with 5 ml of wash soln. (90 ml of $H_2O$ and 10 ml of **I**) and once with $H_2O$. Finally, dissolve the ppt. in a soln. containing a few ml of $H_2O$, 5 ml of 6 *N* HCl and 3 ml of $H_2O_2$ (1:2). Transfer the soln. to a 100-ml calibrated flask, add 9 ml of 6 *N* HCl, and make up to volume. Photometric measurement is made by the usual method.

CHEM. ABSTR.

3015. **Colorimetric determination of small amounts of titanium (IV) in the presence of large amounts of iron (III).** P. Szarvas and B. Csiszár (*Magyar Kém. Foly.*, 1955, **61** [2], 50–54).—Ferric ions (and also $Fe^{\cdot\cdot}$ and $V^{\cdot\cdot\cdot\cdot\cdot}$) form an almost colourless complex with EDTA (disodium salt) (**I**), which is stable towards tiron (disodium catechol-3:5-disulphonate), hence it does not interfere with the determination of the $Ti^{\cdot\cdot\cdot\cdot}$ - tiron complex below pH 6. *Procedure*—To a 1-ml sample of ≃ 2 *N* $H_2SO_4$ soln. containing 3 to 100 μg of $Ti^{\cdot\cdot\cdot\cdot}$ per ml and 0 to 10 mg of $Fe^{\cdot\cdot\cdot}$ per ml, there are added, in this order, 5 ml of 1 per cent. tiron soln., 5 ml of 0·05 *M* **I** and 10 ml of *M* Na acetate, and the soln. is diluted to 25 ml with water, bringing the pH to 5·6. Another sample is prepared similarly, but without tiron, and the two solutions are determined photometrically, at 420 mμ, using an S42 filter and 1-cm cells. The calibration curve, obtained from 1-ml portions containing 6·6 to 132 μg of $Ti^{\cdot\cdot\cdot\cdot}$, obeyed the Beer - Lambert law. With 3·3 μg of $Ti^{\cdot\cdot\cdot\cdot}$ and 10 mg of $Fe^{\cdot\cdot\cdot}$ the error is ± 6 per cent.; a smaller excess of $Fe^{III}$ gave better results.

A. G. PETO

3016. **Polarographic study of sulphuric acid solutions of titanium and niobium.** E. I. Krylov, V. S. Kolevatova and V. A. Samarina (*Dokl. Akad. Nauk, SSSR*, 1954, **98** [4], 593–595).—Titanium and niobium present together in 70 per cent. $H_2SO_4$ solution can be determined polarographically; gelatin, to a concn. of 0·0125 per cent., should be added to the solution. The processes are: $Ti^{\cdot\cdot\cdot\cdot} + e \rightarrow Ti^{\cdot\cdot\cdot}$, and $Nb^{\cdot\cdot\cdot\cdot\cdot} + 2e \rightarrow Nb^{\cdot\cdot\cdot}$, the values of $E_{\frac{1}{2}}$ being − 0·574 and 1·0545 V, and of the diffusion coefficients 0·550 and 0·435 × $10^{-5}$ sq. cm per sec., for $Ti^{\cdot\cdot\cdot\cdot}$ and $Nb^{\cdot\cdot\cdot\cdot\cdot}$, respectively.

R. TRUSCOE

3017. **Determination of zirconium in magnesium alloys by using *p*-bromo- or *p*-chloro-mandelic acid.** R. A. Papucci and J. J. Klingenberg (*Anal. Chem.*, 1955, **27** [5], 835–836).—The magnesium alloy (0·25 to 2 g) is attacked with HCl (1 + 4) or $H_2SO_4$ (1 + 4) (20 to 160 ml) and, after filtration, the soln. can be examined for acid-soluble Zr. The residue is ignited at 1000° C, fused with $KHSO_4$ (1 to 3 g) and the cooled cake is dissolved in dil. $H_2SO_4$ (1 + 1). In either case, the soln. is treated with 0·1 *M* *p*-chloro- or *p*-bromo-mandelic acid (50 ml per 0·25 g of sample) and, after digestion, the ppt. is filtered off, washed with water and ignited at 1000° C to $ZrO_2$. Results from three magnesium alloys are compared with those from the phosphate and alizarin-red-S methods.

D. A. PANTONY

3018. **Determination of hafnium and zirconium by optical spectrographic analysis.** É. V. Gusyatskaya and A. K. Rusanov (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 75–85).—With arc excitation of a complex mixture containing Hf and Zr, fractional volatilisation of the elements, together with the accompanying changes of arc temperature, cause inaccuracies in the determination of Hf and Zr. Stabilisation of temperature by introduction of elements with low ionisation potential gives low intensities. With $HfO_2$ and $ZrO_2$ alone, better results are obtained, since volatilisation is more uniform and sharp changes in intensity of lines do not occur during the arcing. Concn. of ≃ 1 per cent. of Hf in $ZrO_2$ or of Zr in $HfO_2$ can be determined satisfactorily. Feussner spark excitation is, however, recommended. Standards and samples of the oxides for analysis are prepared from mixtures (3 + 1) of powdered Ag and oxides under a pressure of 2000 kg per sq. cm, heated in air at ≃ 800° C before use. The part of the electrode to be held in a pure graphite cylinder is made of pure Ag. The other electrode is a graphite rod with a conical end. Suitable line-pairs are: for 0·5 to 82 per cent. of Hf, Zr II 2643·4 and Hf II 2641·4, and Zr II 2550·7 and Hf II 2551·4; for 0·5 to 85 per cent. of Zr, Zr II 2643·4 and Hf II 2641·4; and for 6 to 75 per cent. of Zr, Zr II 2550·7 and Hf II 2551·4 A; the probable error is 5 to 6 per cent. Continued sparking of the electrodes has no appreciable effect on the intensities of the lines. The method is economical, since 5 mg of an oxide mixture in a standard can be used to obtain several hundred spectra.

G. S. SMITH

3019. **Determination of thorium by fluorescent X-ray spectrometry.** I. Adler and J. M. Axelrod (*Anal. Chem.*, 1955, **27** [6], 1002–1003).—Rock samples containing more than 0·2 per cent. of thoria can be analysed in ≃ 1 hr. with the use of Tl as internal standard in an X-ray spectrographic method. Measurements are made with a two-channel fluorescent X-ray spectrometer with quartz analysing crystals, Geiger-counter detection and simultaneous integration by scalers operating in parallel. To minimise particle-size effects, the sample is ground with a mixture of silicon carbide and aluminium and then briquetted. For 16 samples containing over 0·7 per cent. of thoria the

average difference from chemical results was 4·7 per cent. of the thoria content with a maximum difference of 9·5 per cent. K. A. PROCTOR

3020. **Separation and determination of thorium and aluminium.** C. V. Banks and R. E. Edwards (*Anal. Chem.*, 1955, **27** [6], 947–949).—Thorium may be separated from Al either by pptn. from acid soln. as the oxalate by oxalic acid in the presence of dimethyl oxalate, and igniting the ppt. at 1000° C, or by extraction by mesityl oxide from an acid soln. containing $LiNO_3$, after which it is determined by a modification of the normal titration with EDTA and Chromazurol S and measurement of the absorbance. It is possible to determine the Al in the aqueous phase remaining after the extraction. The method eliminates the usual pH adjustment at the end-point. A. J. MEE

3021. **New colorimetric method for determining nitrogen trioxide in tower and accumulator sulphuric acid.** A. V. Baleev and M. I. Sipyagina (*Zavod. Lab.*, 1955, **21** [2], 154–156).—The method is based on the diazotisation of sulphanilamide and coupling with 1-ethylaminonaphthalene hydrobromide (**I**), which gives a very stable raspberry-red dyestuff. To determine $N_2O_3$ in tower acid, 1 ml of the acid is placed in a 250-ml flask containing 150 to 200 ml of water. After making the soln. up to the mark, 10 ml are placed in a 100-ml cylinder containing 40 to 50 ml of water; 1 ml of HCl (1 + 1), 5 ml of 0·2 per cent. sulphanilamide solution and 1 ml of 0·3 per cent. **I** solution are added, the solution is mixed and set aside for 10 min. Water is added to make 100 ml and the colour is compared with that of standards, visually or in a photocolorimeter. To determine $N_2O_3$ in accumulator acid, 10 ml are diluted to 500 ml and 5 ml of the dil. solution are used. The standards contain 0·0025 to 0·05 mg for tower acid and one-tenth of this weight for accumulator acid. Salts of Fe, Pb, Al, As and Mn, also Cl, $SO_2$ and $SiO_2$ in concn. 10 times that usually present have no effect on the determination, except that the higher amounts of Fe give a positive error of about 2 per cent. G. S. SMITH

3022. **Colorimetric determination of hypophosphite ions in solution.** G. Gutzeit (U.S. Pat. 2,697,651, Date Appl. 21.12.54).—The method is particularly suitable for hypophosphite determination in nickel-plating baths. It is based on the formation of a blue colour with molybdic acid. An aliquot containing $\simeq$ 20 p.p.m. of hypophosphite is treated with 5 ml of $H_3BO_3$ soln. (4·95 per cent. w/v), 5 ml of $Na_2SO_3$ soln. (2 per cent. w/v) and 5 ml of molybdic acid - $H_2SO_4$ soln. (20 g of molybdic acid in 25 ml of 20 per cent. aq. NaOH soln., diluted to 200 ml with $H_2O$; 50 ml of this soln. are mixed with 12·5 ml of conc. $H_2SO_4$ and diluted to 100 ml). The final mixture is diluted to 100 ml with $H_2O$ and placed on a hot-water bath for 30 min. at 50° C. The resulting colour is measured by means of a Fisher "Electrophotometer" with a No. 650A red filter. Phosphite and organic acid radicals do not interfere. A calibration curve is prepared with known concn. of hypophosphite. CHEM. ABSTR.

3023. **Estimation of hypophosphite and phosphite by means of vanadate. Silver salt catalysis.** G. Gopala Rao and H. Sanke Gowda (*Z. anal. Chem.*, 1955, **146** [3], 167–173).—Both hypophosphites and phosphites can be estimated volumetrically by oxidation to phosphate with a vanadate soln. at the temp. of a boiling-water bath, in the presence of $Ag_2SO_4$ as catalyst. In both cases the oxidation is complete in 20 min. for suitable concn. of $H_2SO_4$ and $Ag_2SO_4$. Excess of oxidising agent soln. is used and, after cooling, the unchanged vanadate is titrated with ferrous ammonium sulphate soln., N-phenylanthranilic acid being used as the indicator. The results are in very good agreement with those obtained iodimetrically. J. H. WATON

3024. **Determination of soluble ortho-, pyro- and tri-phosphate in presence of each other.** L. E. Netherton, A. R. Wreath and D. N. Bernhart (*Anal. Chem.*, 1955, **27** [5], 860–861).—A sample (1 g) containing $PO_4'''$, $P_2O_7''''$ and $P_3O_{10}'''''$ is dissolved in water (250 ml). On suitable aliquots, $PO_4'''$ and total P are determined (*Anal. Abstr.*, 1955, **2**, 2078). A 25-ml aliquot is treated with 50 per cent. aq. NaOH soln. (25 ml) and water (100 ml). After being boiled (45 min.) to hydrolyse the triphosphate, the soln. is cooled and made up to 100 ml with water. A 10-ml aliquot of this is cooled in ice and to it is added ammonium molybdate reagent [3·75 per cent. ammonium molybdate in dil. (3 + 7) $H_2SO_4$ (2 vol.), acetone (3 vol.) and water (3 vol.)] (40 ml) and, after 1 min., the absorption is measured at 430 m$\mu$ and compared with standards; from the data, the $P_3O_{10}'''''$ and $P_2O_7''''$ concn. are calculated. Results are given for the analysis of four synthetic samples containing all three ions. D. A. PANTONY

3025. **New titrimetric determination of pyro- and ortho-phosphates.** T. Kato, Z. Hagiwara, R. Shinozawa and S. Tsukada (*Technol. Rep. Tohoku Univ.*, 1954, **19** [1], 93–103).—A study of phosphates is undertaken and an accurate analytical method is established for the determination of pyro- and ortho-phosphates in commercial substances. Pyrophosphate is determined by pptn. with zinc acetate, dissolving the ppt. in aq. $NH_3$ soln. and titrating with EDTA (disodium salt), with Solochrome black as indicator. Quantitative pptn. of zinc pyrophosphate occurs in the pH range 3·8 to 3·9. The chemical reactions are investigated potentiometrically. Orthophosphate is determined by pptg. magnesium ammonium phosphate, dissolving the ppt. in dil. HCl, adding a measured excess of EDTA (disodium salt) and back-titrating with standard magnesium chloride at 30° to 40° C. R. J. MAGEE

3026. **Complexametric determination of pyrophosphoric acid.** W. Nielsch and L. Giefer (*Z. anal. Chem.*, 1955, **146** [5], 323–326).—Pyrophosphate is pptd. at pH 4·1 by the addition of manganous salts. The manganese pyrophosphate is filtered off, washed and dissolved in an excess of EDTA (disodium salt) solution. The solution is back-titrated with $ZnSO_4$, Eriochrome black T being used as indicator. The concn. of $P_2O_7''''$ must be > 0·2 mg per ml of solution, and the $Mn^{++}$ must be in at least five-fold excess. This procedure is more rapid than the gravimetric determination or the conversion into orthophosphate and subsequent determination, and is sufficiently accurate for industrial purposes. A. J. MEE

3027. **Radiometric determination of small amounts of antimony.** Tomitaro Ishimori and Kaoru Ueno (*Bull. Chem. Soc. Japan*, 1955, **28** [3], 200–202).—A radiometric method is described in which $^{60}Co$ is used for the determination of Sb by the formation of dichlorobisethylenediaminocobaltic hexachlorostibinate $[Co(en)_2Cl_2](SbCl_6)$ (**I**), which, unlike the lead salt, is soluble in acetone. *Procedure*—To 1·5 ml of conc. HCl soln., containing 1 to 0·06 mg of Sb, 3 drops of conc. $HNO_3$ are added. The soln. is

warmed and cooled quickly, then 0·23 to 0·3 ml of a *trans*-dichlorobisethylenediaminocobaltic chloride soln. {0·2 g of $[Co(en)_2Cl_2]Cl$ in 1 ml of 2 *N* HCl, showing an activity of about 0·2 mC of $^{60}Co$ per g of $CoCl_2.6H_2O$} is added and the mixture is set aside overnight. The precipitated **I** is filtered off, washed with water until the washings are colourless, then dissolved in acetone; this soln. is evaporated to dryness with an infra-red lamp. The radioactivity of the residue is measured with a Lauritsen electroscope. The results show a linear relationship between the relative radioactivity and the antimony content; Pb does not interfere unless the ratio of Pb to Sb approaches 1:1. G. R. WHALLEY

3028. **Determination of small amounts of bismuth in lead and antimonial lead alloys.** S. J. Fiander (*Analyst*, 1955, **80**, 476–478).—A rapid method for the determination of small amounts of Bi in Pb and Sb - Pb alloys has been developed, 2:3:7-trihydroxy-9-methyl-6-fluorone (2:3:7-trihydroxy-9-methyl*iso*xanth-6-one) being used as precipitant. For refined Pb, the ppt. is evaporated to fuming with $H_2SO_4$, then treated with $H_3PO_2$ and KI. The colour is measured in a Spekker absorptiometer with Kodak No. 2 filters; a calibration graph is prepared. With antimonial Pb, 10 g of the sample are melted under NaOH in an iron crucible, the temp. is raised to between 800° and 850° C, and $NaNO_3$ is cautiously added until violent action has ceased and the melt is dark yellow. The melt is poured into an iron mould, the slag is removed with water and the lead button is dried and weighed. A portion equiv. to 1 g of the original sample is taken for the procedure already described. A blank determination is made on the reagents. For tin, the sample (10 g) is alloyed with Pb of known low Bi content in an iron crucible and is fused with NaOH. A portion of the resulting button, equiv. to 1 g of the original tin, is subjected to the procedure already described, 1 g of the refined Pb used for alloying being used as blank. A. O. JONES

3029. **Direct photometry on [filter-] paper of vanadium separated chromatographically.** A. Lacourt (*Mikrochim. Acta*, 1955, [4], 824–838).—Factors (ageing of spots, interfering elements, etc.) affecting the direct photometric determination of vanadium revealed as the oxinate ($V^V$), after separation by paper chromatography from solutions containing sodium vanadate in 50 per cent. v/v aq. HCl, are studied. The procedure described is reproducible and is accurate to within $\pm$ 2·8 per cent., provided that V alone is present or the concn. of Ni, Ti or Cr is $\not>$ 200 $\mu$g per 0·005 ml (sample vol.). The method cannot be used in the paper-chromatographic analysis of special steels owing to interference by Cr. To reveal the vanadium spot, the conditioned paper strip is exposed in succession ($\simeq$ 20 sec. each time) to bromine vapour, conc. $NH_3$ soln., and bromine vapour; it is then dried in a stream of air before spraying with a soln. of 8-hydroxyquinoline in acetic acid. The black spot is dried under an i.r. lamp for $\simeq$ 30 min., and the photometer reading is taken immediately. The calculation of the true galvanometer deflection and the construction of the standard reference curves are explained. W. J. BAKER

3030. **Automatic spectrophotometric titration with coulometrically generated titanous ion. Determination of vanadium in titanium tetrachloride.** H. V. Malmstadt and C. B. Roberts (*Anal. Chem.*, 1955, **27** [5], 741–744).—A sample of $TiCl_4$ (10 ml) is hydrolysed in ice-cooled 12 *M* HCl (60 ml) by controlled addition of water (40 ml) under a reflux condenser fitted with a dropping funnel - gas trap. Oxygen and Cl are removed from the soln. by means of a stream of $CO_2$, and the soln. is then reduced coulometrically (Ti cathode - Pt anode) to the appearance of two changes of direction in the absorption - time curve (detected automatically by spectrophotometer at 490 or 760 m$\mu$). The vanadium concn. is deduced from the difference in coulombs (as sec.) required between the two changes of direction, which are stages corresponding to the reductions $V^V$ to $V^{IV}$ and $V^{IV}$ to $V^{III}$. For a range of concn. of V in $TiCl_4$ of 0·01 to 0·23 per cent., an average error of 0·00016 per cent. is claimed. Of possible common impurities only $Fe^{\cdots}$ interfere by slightly masking the inflection points. D. A. PANTONY

3031. **Emission spectrochemical analysis of vanadium and iron in titanium tetrachloride: "spark-in-spray" excitation method.** H. V. Malmstadt and R. G. Scholz (*Anal. Chem.*, 1955, **27** [6], 881–883).—In the "spark-in-spray" technique for direct emission spectrochemical analysis of solutions, an atomiser sprays the solution between two horizontal graphite electrodes, across which a controlled high-voltage spark is applied. The method was used for the determination of V and Fe as impurities in $TiCl_4$, and working curves were plotted for various concentration ranges. Results for these determinations were good compared with results obtained from standard solutions of Fe and V in $TiCl_4$, and indicate further possible general applications of the technique. A. J. MEE

3032. **Colorimetric determination of free sulphur.** F. Burriel-Martí and S. Jiménez-Gómez (*Mikrochim. Acta*, 1955, [4], 839–844).—Methods for determining free S by solvent exchange are reviewed, and the Peyron pyridine - water method has been modified to ensure increased accuracy. *Procedure*—Dissolve the sample (containing $\simeq$ 5 mg of free S) in 5 ml of pyridine by heating (water bath) for 1 hr. at 60° C, with occasional stirring. Filter and pour 1 ml of the filtrate into 7 ml of $H_2O$. Measure the transmission of the colloidal dispersion in a Spekker absorptiometer (1-cm cell) with a green (Ilford No. 604) filter. Beer's law is valid for sulphur concn. of 0·2 to 2·2 mg. The use of a stabiliser (casein gives the best results) in the soln. is not recommended, as no great improvement is obtained. W. J. BAKER

3033. **Determination of sulphur in magnetite and apatite using a Lindberg high-frequency furnace.** U. Fernlund and S. Zechner (*Jernkontor. Ann.*, 1954, **138**, 665–667).—Heat the ore in a stream of oxygen in a high-frequency furnace and titrate the resulting sulphurous acid soln. with $KIO_3$. Use a mixture of 7 parts of zinc shavings and 1 part of $Cr_2O_3$ as accelerator. CHEM. ABSTR.

3034. **Determination of total sulphur content of sedimentary rocks by a combustion method.** M. E. Coller and R. K. Leininger (*Anal. Chem.*, 1955, **27** [6], 949–951).—The method is suitable for rocks containing S as sulphide or sulphate, or both. The optimum combustion temperature for the pulverised sample (0·5 g) is 1310° to 1320° C, and iron millings (0·5 g) and granular Sn (1 g) are added as flux. Oxygen is passed over the heated sample and the $SO_2$ formed is absorbed in alkaline KI - starch solution. This solution is titrated with standard $KIO_3$, and hence the original content of S is calculated. A. J. MEE

3035. **The determination of substances in minute quantity. XI. Determination of sulphide.** T. Kato, S. Takei and K. Ogaswara (*Technol. Rep. Tohoku Univ.*, 1954, **19** [1], 85–92).—The determination of sulphide by the formation, in the presence of $Fe^{III}$, of thionine (Lauth's violet) with *p*-phenylenediamine (**I**), and methylene blue with NN-dimethyl-*p*-phenylenediamine (**II**), is studied. The colour of the thionine or methylene blue remains constant, without being affected by the amount of **I** and **II** or the $Fe^{III}$ added, in the range 0·01 to 0·05 *N* HCl soln. Oxidation products of **I** also give a coloration, but this effect is eliminated by the use of a blank soln. Increase in the amounts of **I** and $Fe^{III}$ added decreases the interfering effect of redox substances. Transmittance is minimum at 20° C. The thionine method is considered superior to the methylene blue method. R. J. MAGEE

3036. **Colorimetric determination of sulphate ion.** J. L. Lambert, S. K. Yasuda and M. P. Grotheer (*Anal. Chem.*, 1955, **27** [5], 800–801).—An aq. sample containing 0 to 400 p.p.m. of $SO_4''$ is passed through a cation-exchange column [26 cm of Amberlite IRC-50(H) in a 50-ml burette], and a 20-ml aliquot is treated with 3·116 per cent. aq. $La(NO_3)_3.6H_2O$ (1 ml) and a measured amount of solid thorium borate - amaranth dye reagent. The mixture is shaken (1 min.) and filtered, and the absorption due to the released dye in the filtrate is measured at 521 m$\mu$. The Beer - Lambert law is valid and results agree with those from the $BaSO_4$ gravimetric method. There is no interference from $Cl'$, $I'$, $F'$ (< 15 p.p.m.), $HPO_4''$ (< 50 p.p.m.), $NO_3'$, $HCO_3'$ (< 20 p.p.m.), $Mg^{++}$, $Zn^{++}$, $K^+$, $Na^+$, $Ca^{++}$, $NH_4^+$, $Fe^{+++}$, $OH'$ (< $10^{-4}$ *N*) and $H^+$ (< $10^{-3}$ *N*). D. A. PANTONY

3037. **Titration of sulphate with barium chloride and an adsorption indicator.** R. Geyer (*Z. anal. Chem.*, 1955, **146** [3], 174–181).—Barium chloride can be used to titrate soln. containing $SO_4''$, a 0·1 per cent. soln. of Na alizarinsulphonate in the pH range 3·0 to 3·6 being used as an adsorption indicator. If the soln. is mixed with an equal vol. of an organic solvent, such as acetone, methanol or ethanol, then the $BaSO_4$ remains as a sol beyond the end-point. Good reproducibility of results is obtained if the conditions of titration are kept constant. The presence of other ions, particularly those of the alkali metals, causes deviations from the theoretical results, so that in most cases an empirical standardisation of the $BaCl_2$ soln. is necessary. Ions of Cu, Al and Fe must be absent, as well as other ter- and higher-valent ions. Cobalt and nickel sulphates can be titrated provided that the amounts used do not exceed 0·1 and 0·2 g, respectively, in a titration soln. of 250 ml. Alkali-metal salts in concn. > 0·1 g per 200 ml cause a deterioration of the colour change at the end-point, although this effect can be reduced to some extent by the addition of $Th(NO_3)_4$ soln. Nevertheless it is recommended that this method should be applied only to the determination of pure soln. of $SO_4''$. Details are given for the estimation of amounts of $SO_4''$ in each of the three ranges 2 to 10 mg, 10 to 50 mg and 50 to 250 mg. J. H. WATON

3038. **Precipitation of barium sulphate from aqueous solutions.** W. G. Cobbett and C. M. French (*Disc. Faraday Soc.*, 1954, [18], 113–119).—The rate of pptn. of $BaSO_4$ was followed by electrical conductivity measurements. The influence of the concn. of $Ba^{++}$ and $SO_4''$, the ratio of [$Ba^{++}$] to [$SO_4''$], and the presence of excess of electrolyte was studied. No visible pptn. occurred below a concn. product [$Ba^{++}$] [$SO_4''$] = $1·59 \times 10^{-8}$, *i.e.*, > 160 times the normal solubility product ($0·962 \times 10^{-10}$). The critical concn. product, above which spontaneous formation of nuclei occurs, was calculated as $1·02 \times 10^{-8}$. For part of the time, the reaction appears to be first order and, in a certain limited number of cases, it subsequently becomes apparently third order. S.C.I. ABSTR.

3039. **Nephelometric determination of sulphate impurity in certain reagent-grade salts.** H. J. Keily and L. B. Rogers (*Anal. Chem.*, 1955, **27** [5], 759–764).—The sample (10 g) of, *e.g.*, $CaCO_3$, KCl or $Na_2CO_3$, is dissolved in water or dil. HCl and the pH is adjusted to 1 with HCl and the vol. to 100 ml with HCl (pH 1) after adding ethanol (20 ml). Turbidity is removed by filtration and to a 20-ml aliquot is added $BaCl_2.2H_2O$ (0·42 g, 30 to 40 mesh), which is dissolved by mechanical stirring. Turbidity is measured nephelometrically after 15 to 60 min. The method is claimed to be of general application over the range 0·2 to 10 p.p.m. D. A. PANTONY

3040. **Coulometric determination of selenium [selenite].** K. Rowley and E. H. Swift (*Anal. Chem.*, 1955, **27** [5], 818–820).—Two modifications of an earlier determination of $SeO_3''$ (*Brit. Abstr. C*, 1948, 109; 1951, 247) are described, and the reactions involved are employed in a coulometric determination. To a standard $SeO_3''$ soln. (10 ml) are added 1·0 *VF* (formula wt. per litre) HCl (5 ml) and $H_2O$ (20 ml) in a coulometric titration cell. Either this soln. is treated with 0·1 *VF* aq. $Na_2S_2O_3$ (10 ml) followed by 1·0 *VF* aq. KI (5 ml) and the excess of $S_2O_3''$ is titrated coulometrically with iodine, or the soln. is treated with 1·0 *VF* aq. KI (5 ml) followed by 0·1 *VF* $Na_2S_2O_3$ (10 ml) and the soln. is titrated as before. Results are improved by using an atmosphere of $CO_2$. D. A. PANTONY

3041. **Analysis of chromium - niobium [and other] alloys by means of the intensity of reflection of $\beta$-radiation.** N. A. Bogdanov and V. F. Funke (*Zavod. Lab.*, 1955, **21** [2], 181–183).—The sample of Nb - Cr alloy is placed on a Plexiglas diaphragm above a Geiger - Müller counter. Immediately below the sample is placed some radioactive $^{204}Tl$ on a lead support and a filter of aluminium foil, 90 mg per sq. cm, between this and the counter. The radiation reflected from the niobium atoms has a greater penetrating power through the filter than that from the chromium atoms. The samples for standards and for analysis are prepared from powders with a particle size of < 0·075 mm, which are first stirred in alcohol for 48 hr. A layer 5 mm thick is placed in a mould, 20 mm in diameter, covered with tissue paper and compressed under a pressure of 3 tons per sq. cm. Only the reflected radiation is received by the counter; the Pb holds back the direct radiation from the $^{204}Tl$. The composition of the standards ranges from 8·89 to 100 per cent. of Nb. The intensity of the radiation varies linearly with the content of Nb, which is determined from a calibration curve. The accuracy is $\simeq$ 2 per cent.; the method is suitable for alloys containing > 3 per cent. of Nb, and the time required is 3 min. With Fe - W alloys, samples prepared by sintering at 50° C below the m.p. give the same results for the content of W as those prepared by briquetting, and the same calibration curve can be used. Cast samples of Fe - W alloys also give the same results

if they are heated first at 1000° C for 3 to 4 hr. The method is recommended for the analysis of other binary alloys, in which the atomic numbers of the components differ sufficiently. G. S. SMITH

3042. **A new method for the gravimetric determination of tungsten; infra-red absorption spectra of tungstates prepared at different pH values.** T. Dupuis (*Mikrochim. Acta*, 1955, [4], 851–858).—Based on the use of solutions of alkaline tungstate (10 to 50 mg of $WO_3$ per 20 ml) and cold, saturated aq. purpureocobaltic chloride $Cl_2[CoCl(NH_3)_5]$, two gravimetric procedures for determining W are described: (*i*) as para-purpureocobaltic tungstate ($2{\cdot}4WO_3.X_2O$), where $X_2 = [CoCl(NH_3)_5]$, at pH 5·1 to 6·8, and (*ii*) as meta-purpureocobaltic tungstate ($4WO_3.X_2O$) at pH 2 to 3·1. Greater accuracy (within ± 0·5 per cent.) is attainable with (*i*), whilst the ppt. is easily sol. in dil. aq. $NH_3$, thus providing a colorimetric determination also; it cannot be used if Fe is present, in which case (*ii*) is obligatory. Besides these two tungstates, there are pptd., at pH 3·9 to 4·5, the tritungstate ($3WO_3.X_2O$) and, at pH 9 in ethanol soln., the normal tungstate ($WO_3.X_2O$), although the composition of these two ppt. is not always constant. These four cobaltitungstates, either pure or in admixture, are best identified by their i.r. powder-spectra between 6 and 15 μ; the critical spectral data are reported. W. J. BAKER

3043. **Gravimetric method of determining tungsten in concentrates and alloy steel.** V. V. Stepin and E. V. Silaeva (*Zavod. Lab.*, 1955, **21** [2], 149–151).—The presence of high concn. of alkali, resulting from a fusion with $Na_2CO_3$ of the insoluble matter in tungsten concentrates, renders the pptn. of $WO_3$ difficult. It is shown that complete pptn. can be obtained by the use of amidopyrine. G. S. SMITH

3044. **Spectrographic determination of tungsten in the residues after the extraction of tungsten from tin - tungsten concentrates.** V. Procházková (*Chem. Průmysl*, 1954, **4**, 127–131).—A method was developed for determining W in the residues containing 0·1 to 2·0 per cent. of $WO_3$. The material, in powder form, was ground to pass a sieve of 0·03-mm mesh, well homogenised, mixed with 2 pt. of water-free $Na_2CO_3$, and filled into the crater of a carbon electrode. A salt of Ge was added as internal standard in preference to a salt of Cd originally used. Spectra were initiated by a condensed low-tension spark, according to Sinclair's method (*Chem. Abstr.*, 1948, **42**, 5280). Lines chosen as representative were those at wavelengths 2946·98, 2947·36 and 2944·40 A. The accuracy of the determinations was within ± 5 per cent. CHEM. ABSTR.

3045. **A new test for uranyl ions based on their redox properties.** F. Lucena-Conde and L. Prat (*Mikrochim. Acta*, 1955, [4], 799–802).—The test depends on the reduction of $UO_2^{\cdot\cdot}$ to $U^{\cdot\cdot\cdot\cdot}$, which are then oxidised with an excess of $Fe^{\cdot\cdot\cdot}$. *Procedure*—To 1 ml of the slightly acid uranyl soln. in a test-tube add 0·5 ml of liquid zinc amalgam and stir. Separate the soln. and to it add one drop each of 1 per cent. aq. $Th(NO_3)_4$ and 5 per cent. aq. $NH_4F$. Centrifuge, and wash the ppt. ($UF_4 + ThF_4$) with $H_2O$ containing $NH_4F$; then add two drops each of 1 per cent. aq. $FeCl_3$ and 5 per cent. aq. $NH_4F$, followed by saturated aq. sodium acetate to adjust the pH, and finally one drop of 1:10-phenanthroline. A red colour indicates $UO_2^{\cdot\cdot}$. If the concn. of $MoO_4''$, $WO_4''$, $VO_3'$ or $Ti^{\cdot\cdot\cdot\cdot}$ is > 9 times that of U, the sensitivity limit is reduced from $pD$ 4·7 to $pD$ 3·0 ($pD = -$ log dilution). W. J. BAKER

3046. **Fluorimetric micro-determination of uranium with morin.** E. Tomić and F. Hecht (*Mikrochim. Acta*, 1955, [4], 896–902).—The rapid procedure described is based on the quenching, proportional to the concn. of $UO_2^{\cdot\cdot}$, of the fluorescence of 0·01 per cent. morin in neutral soln. containing acetone. Interfering ions are removed by extraction of $UO_2^{\cdot\cdot}$ with ether. The accuracy is within ± 5 per cent. for uranium concn. of 0·5 to 10 μg in 10 ml of soln. W. J. BAKER

3047. **Direct spectrographic determination of uranium in aqueous solutions.** R. G. Canning and P. Dixon (*Anal. Chem.*, 1955, **27** [6], 877–880).—The development of a direct spectrophotometric method for the estimation of U in solutions containing U, V, Cr, the rare earths, $Fe^{II}$ and $Fe^{III}$ is described, making use of the strong absorbance peak of $U^{IV}$ at a wavelength of 660 mμ. An unreduced reference solution and a reduced solution are used such that the components other than U are unaltered in the two solutions. Ferrous sulphate in hot 40 per cent. v/v $H_3PO_4$ reduces U and V rapidly from the $U^{VI}$ and $V^{IV}$ to the $U^{IV}$ and $V^{III}$ states. It was found possible to apply a two-wavelength (660 and 700 mμ) method for the determination of U in the presence of V. The reference solution was obtained by oxidising all components with $H_2O_2$, which also destroyed other oxidising agents, such as chlorate and permanganate. The content of V can also be determined, but with less accuracy than that of U. A. J. MEE

3048. **Determination of uranium in uranium concentrates. Use of ethyl acetate.** R. J. Guest and J. B. Zimmerman (*Anal. Chem.*, 1955, **27** [6], 931–936).—Nitric acid solutions of material high in uranium content are extracted with ethyl acetate, $Al(NO_3)_3$ being used as a salting-out agent. The uranium is then determined colorimetrically by the NaOH - $H_2O_2$ method. Methods have been evolved to eliminate the effect of the interference of Th in the colorimetric measurement. A. J. MEE

3049. **Radio-isotopic study of uranium separations: separations by filter-paper partition chromatography with tetrahydro-2-methylfuran.** H. P. Raaen and P. F. Thomason (*Anal. Chem.*, 1955, **27** [6], 936–944).—An application of radioactive tracer technique, including autoradiography and α-radiation counting, to the micro-separation of U from 31 other metals by filter-paper chromatography with tetrahydro-2-methylfuran, is described. Information is supplied on the identification of the $U^{VI}$ locus; the sorption gradient of the U and solvent-phase separation on the filter-paper strip (determined by α-count measurements of the chromatograms); acidity differentials along the strip; effect of the age of the eluting solvent; optimum conditions for isolating the U band on the chromatogram; the efficiency of the method for the separation of U from other metals; and the quant. elution of U from the chromatogram. Of the radio-isotopes studied, $^{106}Ru$, $^{106}Rh$ and $^{185}W$ were not completely separated from $^{233}U$, and the results for $^{113}Sn$ and $^{124}Sb$ were not conclusive. A. J. MEE

3050. **Determination of microgram and submicrogram quantities of uranium by neutron-activation analysis.** H. A. Mahlman and G. W. Leddicote (*Anal. Chem.*, 1955, **27** [5], 823–825).—The principles of neutron-activation analysis and

treatment of irradiated specimens containing 0·0001 to 0·1 μg of U per g are discussed and the following procedure for the determination of U is described. The sample and a comparable standard are irradiated with 0·0252 ev. neutrons and then allowed to decay (4 hr.). The isolation of $^{239}Np$ is effected as follows. The treated sample is dissolved by standard procedures and the soln. is heated to fumes of $H_2SO_4$. From this soln. $^{239}Np$ is co-pptd. with $La^{\cdots}$, first with aq. $NH_3$ and then with $F'$ in the presence of hydroxylamine, $Sr^{\cdot\cdot}$ and $ZrO^{\cdot\cdot}$ being used to assist retention of other radio-isotopes in soln. After four such pptn., the fluoride ppt. is extracted with $M$ $HNO_3$ and the activity of the extract is measured by a γ-scintillation counter. By comparison of corrected $^{239}Np$ activities with those of similarly treated standards, the concn. of U is deduced specifically with a precision of ± 10 per cent. at the 0·1-μg level. Results are presented for three uranium ores and three uranium soils.

D. A. PANTONY

3051. **Retention of uranium during oxidative ashing of selected naturally occurring carbonaceous substances.** F. Cuttitta and E. Brittin (*U.S. Atomic Energy Comm.*, TEI-461, 1954, 8 pp.).—The routine determination of U in natural carbonaceous materials includes an oxidative ashing. This method was compared with a low-temp. wet-oxidation method. There was no appreciable loss of U by direct ashing. N. E.

3052. **An improved acidimetric determination of fluoride.** J. M. Chilton and A. D. Horton (*Anal. Chem.*, 1955, **27** [5], 842–844).—The sample containing ≃ 5 mg of $F'$ is distilled in the presence of $SiO_2$ and $HClO_4$ by standard methods. The distillate is made alkaline with NaOH and evaporated to a vol. of 2 to 3 ml. After adjustment to pH < 1 with conc. HCl in an automatic pH titration cell, the mixture is treated with 2 to 3 g of NaCl in excess of saturation and an equal vol. of ethanol is added. At 50° to 60° C, $N$ NaOH is added to adjust the pH to ≃ 7. After final adjustment to pH 7·0 ± 0·5, the soln. is titrated automatically with standard potassium alum soln. The end-point is taken as the inflection in the graph of pH against ml of titrant, and at equivalence $Al^{\cdots} \equiv 6F'$. Interference due to $NH_4^{\cdot}$ and certain heavy-metal cations is eliminated by a preliminary treatment with aq. NaOH soln. Difficulties due to the presence of B are avoided by a fusion with $Na_2CO_3$. At the 5-mg level, an error of ± 0·2 per cent. is claimed.

D. A. PANTONY

3053. **Direct potentiometric titration of fluorides.** M. M. Raïnes, O. I. Pirogova and M. V. Andreeva (*Zavod. Lab.*, 1955, **21** [2], 152–154).—Titration is carried out with a smooth platinum electrode and a saturated calomel electrode in 50 ml of solution containing 1 to 15 mg of $F'$, with 0·1 $N$ thorium nitrate solution as titrant. The important factors are pH 6 to 7, washing of the platinum electrode after each titration with dilute $KMnO_4$ solution, and complete removal of $CO_2$ from the solution.

G. S. SMITH

3054. **Determination of small and large amounts of fluorine in rocks.** F. S. Grimaldi, B. Ingram and F. Cuttitta (*Anal. Chem.*, 1955, **27** [6], 918–921).—A flux method for the decomposition of silicate rocks is described. The sample is fused with a mixture of $Na_2CO_3$ and ZnO, leached with water and filtered; fluorine in the filtrate is distilled directly from a $HClO_4$ - $H_3PO_4$ mixture. This technique permits the quant. distillation of F in the presence of much Al; in previous methods Al greatly retarded distillation. Fluorine in the distillate is determined either by micro-titration with thorium nitrate or colorimetrically with thoron. Phosphate does not interfere with the determination.

A. J. MEE

3055. **Rapid determination of chlorine in electrolytic solutions.** A. A. Salin, O. Ya. Chaunina and R. A. Chernova (*Zavod. Lab.*, 1955, **21** [2], 163–164).—A known potentiometric method is applied to the determination of chloride in electrolytic solutions. The indicator electrode is a silver wire, 1 mm in diameter, the reference electrode is saturated calomel, and titration is carried out with 0·1 $N$ $AgNO_3$. G. S. SMITH

3056. **Rapid determination of perchlorates.** N. L. Crump and N. C. Johnson (*Anal. Chem.*, 1955, **27** [6], 1007–1008).—Perchlorates may be determined by fusion with $Na_2O_2$ in a Parr bomb. The chloride formed is determined volumetrically by the standard Volhard method. Quant. results are also obtained on a micro scale, and it is suggested that the method, which is applicable to all types of perchlorates, may be adapted to routine analysis. A. J. MEE

3057. **The use of chlorine dioxide solution. I. Oxidimetric determination of iodides in the presence of bromides and chlorides.** S. Škramovský, Z. Tauer and J. Novotný (*Chem. Listy*, 1954, **48** [9], 1335–1337).—Iodides can be determined by potentiometric titration of their solutions in dil. HCl or $H_2SO_4$ with 0·01 $N$ $ClO_2$ in glacial acetic acid, according to the equation—

$$2ClO_2 + 10I' + 8H^{\cdot} \rightleftharpoons 5I_2 + 2Cl' + 4H_2O.$$

A 10,000-fold excess of $Cl'$ and a 400-fold excess of $Br'$ do not interfere, but all anions reacting with $I'$, as well as $NO_3'$, $Fe^{\cdot\cdot}$, $As^{\cdot\cdot\cdot}$, $Sb^{\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Sn^{\cdot\cdot\cdot\cdot}$ and much $Cr^{\cdot\cdot\cdot}$, must be absent. The method has been applied to the analysis of pharmaceuticals, with results in good agreement with those from the usual argentimetric and manganimetric procedures. To prepare the reagent, heat a mixture of cryst. oxalic acid (150 g), $KClO_3$ (40 g) and $H_2O$ (20 ml) at 60° C, condense the evolved $ClO_2$ and dissolve the liquid product in glacial acetic acid to give a 0·01 $N$ soln., which is standardised iodimetrically. When kept at room temp. in a dark-glass container, the reagent is fairly stable. G. GLASER

3058. **The use of chlorine dioxide solution. II. Titration [of iodide] in acetic acid.** S. Škramovský, Z. Tauer and J. Novotný (*Coll. Czech. Chem. Commun.*, 1955, **20** [3], 718–720).—An approx. 0·005 $M$ solution of $ClO_2$ in 0·1 $M$ ammonium acetate (10 ml) may be standardised by potentiometric titration with 0·01 $M$ quinol in acetic acid:

$$2ClO_2 + C_6H_4O_2 = C_6H_4O_2 + 2HClO_2.$$

Iodide, in glacial acetic acid medium, may be determined in the presence of small amounts of chloride and bromide by potentiometric titration with $ClO_2$ in acetic acid. [This is a translation into German of a paper originally published in *Chem. Listy*, 1955, **49**, 141.] A. R. ROGERS

3059. **The determination of small amounts of manganese dioxide.** W. Geilmann and K. Beyermann (*Z. anal. Chem.*, 1955, **146** [4], 254–260).—A micro-adaptation of the classical method for the determination of $MnO_2$ with HCl, distillation of Cl into KI and titration of I with $Na_2S_2O_3$, is described. The titration is best carried out electrometrically.

The accuracy is satisfactory. Tables of results are given. Experiments with $PbO_2$ have shown that the method can be used for other dioxides.

R. STERN

3060. **The separation of iron, cobalt, zinc and phosphorus on synthetic resin.** H. L. Helwig, J. K. Ashikawa and E. R. Smith (*U.S. Atomic Energy Comm.*, UCRL-2655, 1954, 11 pp.).—The separation of trace elements from neutron- or cyclotron-irradiated biological tissue is facilitated by using an anion-exchange resin. Dowex 1 was washed in a column with several litres of 0·5 *N* and 5 *N* HCl, then immersed in 5 *N* HCl. The washed resin was packed into a column of 1·4 sq. cm cross-sectional area to a height of 12 to 24 cm and equilibrated with 12 *N* HCl. Carrier salts were prepared by dissolving 0·625 g of Fe, 0·625 g of Zn and 0·125 g of Co in moderately strong HCl. $^{59}Fe$, $^{60}Co$, $^{65}Zn$ and $^{32}P$ were added to the salts and the soln. was evaporated almost to dryness; 2 to 3 drops of conc. $HNO_3$ were added before completely drying. The oxides were converted into chlorides by adding a few drops of HCl, heating to dryness and diluting to 25 ml with 12 *N* HCl. Two ml of this solution were transferred to the resin column. The P was slightly adsorbed and was eluted with 12 *N* HCl. Cobalt, Fe and Zn were eluted with 50 ml each of 4 *N*, 0·5 *N* and 0·005 *N* HCl, respectively. Copper and gallium have been found in the iron-containing fraction. On the basis of decay rates the recovery of radioactive components was better than 98 per cent. with no indication of cross contamination in the Co, Fe and Zn fractions. The P fraction was contaminated with a long-life component; colorimetric analysis of this fraction for Co, Fe and Zn gave negligible results.

CHEM. ABSTR.

3061. **Measurement of the intensity of reference lines for the analysis of iron, nickel or cobalt alloys.** W. Marti (*Mikrochim. Acta*, 1955, [2–3], 657–661).—Intensity curves are obtained from two series of alloys with varying contents of Fe, Co and Ni. The curves are used in the quantometric spectral analysis of highly alloyed steel and also of nickel and cobalt alloys for correcting the basic metal content.

D. R. GLASSON

3062. **Spectrochemical determination of rare elements in steel.** C. G. Carlsson and A. Larsson (*Jernkontor. Ann.*, 1954, **138**, 737–743).—The d.c. method, the carrier method and the double-arc method were used. After the samples had been dissolved in HCl, the bulk of the Fe was removed by a double ether-extraction, first as $Fe^{++}$, then as $Fe^{+++}$. The ether soln. from the first extraction, containing Ga, Mo and other elements, and the aq. soln. from the second extraction were used for analysis. The resulting soln. were analysed spectrographically after evaporation on pure carbon electrodes. Germanium was determined separately by this method after it had been pptd. as sulphide from an $H_2SO_4$ soln., with Cu as a carrier element.

CHEM. ABSTR.

3063. **Determination of traces of nickel and zinc in copper and its salts.** L. Meites (*Anal. Chem.*, 1955, **27** [6], 977–979).—A method by which as little as $10^{-5}$ per cent. of Ni or Zn may be determined in Cu and its salts is described. An ammoniacal solution of the sample is electrolysed, using a mercury cathode maintained at a constant potential sufficient for the complete reduction of Cu to the metallic state, but insufficient to affect either Ni or Zn, which are determined polarographically in the residual solution.

A. J. MEE

3064. **Determination of traces of nickel. I.** W. Oelschläger (*Z. anal. Chem.*, 1955, **146** [5], 339–345).—In the determination of nickel with dimethylglyoxime (**I**) the preliminary oxidation of $Ni^{II}$ to $Ni^{IV}$ with bromine water in aq. $NH_3$ soln. has disadvantages and gives unreliable and inconsistent colours. The following procedure is recommended. To an aliquot part of a soln. in HCl are added 20 per cent. Na citrate soln. (10 ml), 10 per cent. hydroxylamine hydrochloride soln. (2 ml) and 1 per cent. alcoholic soln. of **I** (2 ml); the soln. is neutralised to phenolphthalein with conc. aq. $NH_3$ and 3 drops are added in excess. If the soln. is turbid, more Na citrate soln. is added until it clears. After dilution with $H_2O$ to 60 ml, the soln. is extracted with $CHCl_3$ (20 ml); the chloroform extract is washed twice with aq. $NH_3$ soln. (1:50), and then shaken with 0·5 *N* HCl (15 ml). The separated acid soln. is treated with a 2·5 per cent. soln. of **I** in *N* NaOH (2 ml), 10 *N* NaOH (1 ml) and 10 per cent. $(NH_4)_2S_2O_8$ soln. (0·3 ml). After about 10 min. the soln. is diluted to 25 ml and the absorption is measured at 460 mμ. Directions are given for removing traces of Ni from the reagents. N. E.

3065. **Determination of traces of nickel in substances containing iron and manganese. II.** W. Oelschläger (*Z. anal. Chem.*, 1955, **146** [5], 346–350).—The influence of certain elements on the micro-determination of Ni with dimethylglyoxime (see *Anal. Abstr.*, 1955, **2**, 3064) is studied. Iron and cobalt do not interfere. Copper forms a complex with dimethylglyoxime; by increasing the volume of hydroxylamine hydrochloride soln. to 10 ml, Cu up to 5 mg causes no error, but larger amounts give high results. In the presence of Mn (50 to 100 mg) the procedure in Part I (see above) is modified; 5 ml of 10 per cent. $NH_2OH.HCl$ soln. are used and the $CHCl_3$ extract is shaken 3 times with 10 ml of aq. $NH_3$ soln. (1:200). Good results are obtained for 10 μg of Ni in the presence of a mixture of Mn (100 mg), Fe (100 mg) and Cu (5 mg).

A. J. MEE

3066. **Determination of hydrogen-ion concentration in nickel electrolytes by a potentiometric method.** E. I. Ishutchenko, V. S. Ogienko and V. G. Shipunova (*Zavod. Lab.*, 1955, **21** [2], 164).—The nickel electrolyte is placed in a glass tube closed at one end with a rubber stopper carrying a platinum-plate electrode joined to a copper wire through the stopper. The other end is fitted with a ground-glass stopper. The tube is placed vertically in a vessel containing 0·1 *N* citric acid so that connection is made between the electrolyte and the citric acid through the ground-glass stopper. A second tube of similar length, with a rubber stopper carrying a platinum-plate electrode at its lower end making contact with the solution, and connected with a copper wire which passes up through the tube, is also placed in the vessel. The two electrodes serve for the determination of pH by Gonashvili's method (*Zavod. Lab.*, 1949, **15**, 7), but without the need for an agar - agar connection.

G. S. SMITH

3067. **Potentiometric and conductimetric titrations of free acids and of acids liberated by hydrolysis from nickel (II) salts at high temperatures.** F. Čůta, Z. Ksandr and M. Hejtmánek (*Chem. Listy*, 1954, **48** [9], 1341–1345).—Conditions for the separation of pure $Ni(OH)_2$ from some $Ni^{II}$ salts at high temp. are described and discussed. By potentiometric

and conductimetric titrations it is possible to determine free acid in the presence of a $Ni^{II}$ salt at 25° C. By titrating $Ni(ClO_4)_2$ and $Ni(NO_3)_2$ with NaOH soln. at 90° C, the total acid liberated by hydrolysis can be determined, whilst only 99 and 97 per cent. of the acid liberated from $NiCl_2$ and $NiSO_4$, respectively, can be determined in this way. At temperatures below 50° C the hydrolysis is incomplete. Low results are caused by the formation of sparingly soluble basic salts. G. GLASER

3068. **Ferricyanide titration of cobalt using ethylenediamine.** H. Diehl and J. P. Butler (*Anal. Chem.*, 1955, **27** [5], 777–781).—Cobalt (5 to 30 mg) in cobalt bronze, stainless steel, Cr - V - Mo steel and stellite is determined, after dissolution in $HNO_3$ or $HNO_3$ - HCl and fuming with $HClO_4$ (5 ml), dilution with water and addition of ethylenediamine (2·5 to 5 ml), by potentiometric titration under N with standard $K_3Fe(CN)_6$, in the presence of citrate or sulphosalicylate as complexing agent, either directly or by back-titration of an added excess of $Fe(CN)_6'''$ with standard $Co''$. No interference results from $Cr'''$, $V^{V}$, $Mo^{VI}$, $Ag^{+}$, $W^{VI}$, $Be''$, $Cu''$, $Mn''$, $Ni''$ and $Nb^{V}$. The method can be extended to the determination of $Mn''$ unless much $Fe'''$ is present. D. A. PANTONY

3069. **Titrations involving cobalt in ethylenediamine solutions.** J. P. Butler (*Iowa St. Coll. J. Sci.*, 1955, **29**, 388–389).—A method involving the use of ethylenediamine (**I**) rather than $NH_3$ as the complexing agent in the ferricyanide titration of Co is described. The sample is dissolved in aqua regia, fumed with $HClO_4$ to remove $HNO_3$, cooled, diluted, and boiled for several min. Citrate or sulphosalicylate is then added to prevent pptn. of other metal hydroxides, followed by **I**. The solution is then titrated with 0·01 *N* $K_3Fe(CN)_6$ potentiometrically, platinum and saturated calomel electrodes being used. The use of solutions of $CoSO_4$ in **I** as reducing agent for org. and inorg. compounds was also studied in detail. It is concluded from the results that this is unlikely to provide useful methods of quant. estimation, except with permanganate, when the addition of the sample to acid ferricyanide solution, followed by back-titration, gave satisfactory results. S.C.I. ABSTR.

3070. **Volumetric method of determining cobalt with dimethylglyoxime.** A. K. Babko and M. V. Korotun (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 100–106).—To titrate $Co''$ in pure salts, the neutral solution is treated with 2 g of $NH_4Cl$ and excess of aq. $NH_3$ soln. and diluted to a vol. of 50 to 70 ml. In the presence of tervalent metals the original solution is treated with 10 ml of conc. HCl and 15 g of $Na_4P_2O_7$, heated to between 70° and 80° C, cooled, and mixed with excess of aq. $NH_3$ soln. In the presence of Ni, the titration will give the sum of Co and Ni. The solution is titrated slowly, with vigorous shaking, with dimethylglyoxime solution (11·6 g dissolved in 200 ml of *N* NaOH and diluted to one litre), a drop being withdrawn from time to time and placed on a strip of filter-paper resting on indicator paper, prepared by dipping paper in an ammoniacal solution of $Ni''$ and drying in air. The end-point is shown by a pink spot on the indicator paper. To titrate Ni in the presence of Co, 1 to 1·5 g of ammonium persulphate are added to the solution (25 to 30 ml) treated with 10 to 12 g of $NH_4Cl$ and 7 to 8 ml of conc. aq. $NH_3$. After 10 min. the oxidation of the Co is completed by heating, and excess of the oxidant is destroyed by boiling. The cooled solution is nearly neutralised with HCl, diluted to a vol. of 50 to 70 ml and titrated without filtration with dimethylglyoxime solution, paper treated with the reagent being used as an external indicator. Cobalt cannot be determined satisfactorily by continuing the titration in the same solution with $Ni''$-treated paper as indicator. The method is applied to the determination of Ni and Co in solutions containing Fe, Cr and other elements, which are first pptd. by means of ZnO.

G. S. SMITH

3071. **Polarographic determination of palladium.** R. F. Wilson and R. C. Daniels (*Anal. Chem.*, 1955, **27** [6], 904–906).—A graphical method for the precise evaluation of diffusion currents obtained in a polarographic estimation of $Pd^{II}$, which are proportional to the actual concentration of Pd, is described. The optimum conditions are obtained in an aq. $NH_3$ - ammonium chloride buffer. It is found that accuracy is lost in the presence of Pt, Ir and Rh ions, but separation is achieved by the use of dimethylglyoxime. The interference of certain associated base metals, $Au^{III}$, $Ag^{I}$, $Cu^{II}$, $Cr^{III}$, $Fe^{III}$, $Ni^{II}$ and $Ti^{III}$, was studied. In general, the polarographic method displays a fair degree of tolerance for these ions. A. J. MEE

3072. **The applications of polarography to the analysis of electroplating solutions.** R. Diaz (*Plating*, 1955, **42** [4], 415–416).—The literature of polarography related directly to the analysis of electroplating solutions is reviewed, and references are given covering the analysis of these solutions for major and minor constituents. (21 references.)

N. E.

3073. **Spectrochemical analysis of igneous rocks, sediments and ores.** S. Landergren and W. Muld (*Mikrochim. Acta*, 1955, [2–3], 245–250).—The samples for analysis are pulverised and divided into three parts: (*a*) for the determination of major constituents, the material (0·2 g) is homogenised by fusion with $Li_2CO_3$ (0·5 g) and $H_3BO_3$ (0·9 g) at 1000° C for 10 to 20 min. in a graphite crucible, and then analysed spectrographically by the high-tension spark and air - acetylene flame methods; (*b*) for minor constituents, the carbon-arc cathode-layer method is used, either in its original or a modified form; (*c*) for special analyses, *e.g.*, for Au, a solution of the sample is evaporated on a heated carbon-rod anode and the spectrum is emitted by means of a d.c. interrupted arc. D. R. GLASSON

See also Abstracts 2933, 2935, 2936, 2937, 2940, 2948, 3088, 3242, 3257.

## 3.—ORGANIC ANALYSIS

3074. **Rapid methods of micro-analysis. Simultaneous determination of elements by decomposition of organic substances by heating with metallic potassium.** M. O. Korshun and M. N. Chumachenko (*Dokl. Akad. Nauk, SSSR*, 1954, **99**, 769–771).—The specimens are heated with K at 80° to 85° C in a micro-bomb (illustrated) with a hemispherical plug closure; this serves to decompose various organic substances within a few min. Halogens are converted into potassium halides, S into $K_2S$, most of the carbon content is left as C and part may be converted into cyano derivatives, and Hg is eliminated as free metal. The determination of Cl′, Br′ and I′ may be made argentimetrically, but the mercurimetric method for Cl′ and Br′ and the iodimetric for I′ (diphenylcarbazone indicator) are preferred. If N

and S are also present, an aliquot is oxidised with $KMnO_4$ to remove interfering KCN and $K_2S$ before the halogen determination; the $KMnO_4$ is destroyed with $H_2O_2$. For the determination of halogens and Hg, the aq. mixture is filtered, the Hg is dissolved in $HNO_3$, treated with excess of NaCl, and back-titrated with $Hg(NO_3)_2$. Direct iodimetric titration of S usually gives low and variable results, owing to oxidation of the sulphide by air, but results are satisfactory if the soln. is strongly alkaline (15 per cent. KOH); N and the halogens do not interfere. The error for halogens, Hg and S is $\pm$ 0·2 per cent.
CHEM. ABSTR.

3075. **The micro-Kjeldahl determination of nitro nitrogen.** P. R. W. Baker (*Analyst*, 1955, **80**, 481–482).—It has been shown by White *et al.* (*Brit. Abstr. C*, 1951, 399) that their sealed-tube micro-Kjeldahl method cannot be used for N linkages requiring reduction before the usual digestion. It is now found that the reduction of nitro compounds can be conveniently effected by the addition of 50 mg of *o*-mercaptobenzoic acid or glucose to the digest (25 mg are insufficient). The temp. of 470° C used by White *et al.* (*loc. cit.*) is dangerously high, and satisfactory results were obtained by digestion with HgO and $H_2SO_4$ at 420° to 440° C for $\simeq$ 45 min. It was found that many nitro compounds gave correct results without reduction and it appears that if the compound contains the group $-C{\cdot}C_6H_4{\cdot}NO_2-$ no reduction is necessary. The behaviour of *o*- or *m*-nitrophenyl compounds has not yet been fully investigated. Oximes and N-oxides do not normally require reduction (dimethylglyoxime with its relatively high content of N is an exception). For compounds containing N–N linkages, glucose is slightly more efficient than *o*-mercaptobenzoic acid, but with neither reagent do the results approach the theoretical values. Examples are given of results with compounds not requiring reduction, and of the improvement in the yield of N when the above-mentioned reducing agents are used with compounds requiring reduction. A. O. JONES

3076. **Determination of microgram quantities of organic nitrogen.** J. P. Dixon (*Anal. Chim. Acta*, 1955, **13** [1], 12–15).—The method described is of wide applicability. The sample, $\not>$ 200 mg and containing $\simeq$ 0·1 mg of N, is digested in weighed amounts of $H_2SO_4$ and of a catalyst comprising a mixture of $K_2SO_4$, HgO and Se (30:2:1). For some N-containing material, pretreatment with HI and red P is necessary. The $NH_3$ is distilled off in a micro-Kjeldahl unit into a 1 per cent. soln. of HCl. To the distillate are added NaOBr soln. and sufficient of a KOH - $H_3BO_3$ buffer soln. to bring the pH to between 8·5 and 9·6. After a few sec., KI and acetic acid soln. are added, and the excess of NaOBr is determined iodimetrically with 0·002 *N* $Na_2S_2O_3$ soln., sodium starch glycollate being used as indicator. A blank is performed on accurately measured amounts of reagents. J. H. WATON

3077. **Micro-estimation on paper of catalytic activity. I. Ultramicro-determination of organic iodine.** S. Lissitzky (*Bull. Soc. Chim. Biol.*, 1955, **37** [1], 89–96).—A Whatman No. 4 paper is cut so that six strips hang from a common portion, which is bent into a circle. Known quantities of a standard solution of the iodine-containing compound are deposited at the ends of five of the strips, and a sample of the solution to be estimated at the end of the sixth strip. The paper is suspended so that the ends of the strips dip into a dish containing a solution of $Ce(SO_4)_2$ and $Na_3AsO_3$, which is allowed to migrate to the top of the strips; the paper is dried, and examined under u.v. light. On each strip there is a zone where $Ce^{IV}$ has been reduced to $Ce^{III}$, the size of the zone being dependent on the amount of I; this zone is fluorescent, and its area on each strip is estimated by weight or by planimetry. The unknown concentration of I is then determined by interpolation, with a precision of $\pm$ 5 per cent. The method is applicable to I′, $IO_3$′, $IO_4$′ and to iodinated derivatives of tyrosine and thyronine; by suitable choice of concn. in the reacting solution a linear calibration plot is obtained for 0·05 to 1·50 $\mu$g of amino acid. The method is applicable to the products of the hydrolysis of thyroglobulin, after chromatographic separation. H. P. PAGET

3078. **Micro-detection and colorimetric determination of arsenic in organic compounds by decomposition with magnesium.** M. Jureček and J. Jeník (*Coll. Czech. Chem. Commun.*, 1955, **20** [3], 550–554).—A rapid method is described for the detection and colorimetric determination of free and combined arsenic in organic compounds. The sample (50 $\mu$g to 50 mg) is heated in a sealed tube for 5 min. with a mixture (3 + 1) of Mg and MgO, which converts all the arsenic into magnesium arsenide. The tube is opened, and the contents are decomposed by dil. $H_2SO_4$. Arsine is evolved, and is absorbed in a 0·5 per cent. soln. of silver diethyldithiocarbamate in pyridine. The colour produced has an absorption max. at 560 m$\mu$, and is proportional to concn. up to 20 $\mu$g of As in 3 ml of soln. [This is a shortened version in German of papers originally published in *Chem. Listy*, 1954, **48**, 1771, and 1955, **49**, 264.] A. R. ROGERS

3079. **A rapid determination of oxidation values of non-volatile organic compounds by the iodic acid decomposition method.** Shigeru Ohashi (*Bull. Chem. Soc. Japan*, 1955, **28** [3], 171–176).—The apparatus and procedure for the determination of oxidation values, defined as the number of oxygen atoms required to oxidise completely 1 mol. of an organic compound, are described. *Procedure*—The sample (15 to 100 mg) is placed in a reaction flask containing 3 to 5 ml of phosphoric acid ($d$ = 1·7) (previously dehydrated at 300° C) and the requisite amount of solid $KIO_3$, and an attached absorption vessel is filled with 10 to 20 ml of a 0·1 *N* $Na_3AsO_3$ soln. The flask is heated to between 80° and 240° C and all the iodine liberated is swept by dry air into the absorption vessel. When the reaction is complete, the flask is cooled, water (10 to 15 ml) is added and heating is effected until all the dissolved I is removed and absorbed in the $Na_3AsO_3$ soln. The absorption vessel is disconnected, $NaHCO_3$ soln. is added and the excess of $Na_3AsO_3$ is titrated with 0·05 *N* I soln. (starch indicator). Each determination requires 20 to 30 min.; the accuracy is $\pm$ 1 per cent. G. R. WHALLEY

3080. **The determination of alkoxy groups.** W. Kirsten and S. Ehrlich-Rogozinsky (*Mikrochim. Acta*, 1955, [4], 786–798).—In the new improved apparatus and procedure described and illustrated, the sample (3 to 15 mg) is heated for 30 min. at 100° C (steam-bath) with 2 ml of the reaction mixture in a glass-stoppered tube, which is afterwards opened and the contents transferred to a

distillation unit. By boiling for from 12 to 60 min., the alkyl iodide is liberated and is absorbed in 5 ml of a soln. of acetic acid and potassium acetate containing 10 drops of bromine; HI is removed in a $KHCO_3$ scrubber. The contents of the absorption tube and the wash-water are transferred to a 100-ml flask, 2 ml of sodium acetate soln. (40 per cent. w/v) plus 10 drops of 99 per cent. formic acid are added, followed, after vigorous shaking and an interval of 2 min., by 3 ml of 10 per cent. w/v alkaline KI soln., and then subsequent titration with 0·05 *N* $Na_2S_2O_3$. The reaction mixture is prepared by refluxing red phosphorus (2 g), phenol (60 g), HI (*d* 1·7) (100 g) and propionic acid (5 ml) for ≃ 30 min. in a slow stream of nitrogen, and gently boiling for another 15 min. before pouring the hot soln. into a Pyrex-glass bottle. The use of phenol containing propionic acid as solvent for both sample and alkyl iodide, and of red phosphorus for preventing the formation of free I and ensuring complete reaction of samples containing large amounts of oxidising agents, obviates the troubles often occuring in the older procedures. Results (reported) for different solid, highly insol., S-containing and very volatile compounds, respectively, indicate a mean error of ⩾ ± 0·5 per cent., except for *iso*propoxy compounds, which give very low values. W. J. Baker

3081. **Estimation of small amounts of trichloroethylene and trichloroacetic acid.** B. Souček and E. Franková (*Pracovní Lék.*, 1952, **4**, 264–273).—As absorbent for trichloroethylene (**I**), a mixture of pyridine, water and 15 per cent. NaOH soln. (61·54:38:0·46) is superior to previously used solvents since it does not contain excess of alkali. **I** was removed from water containing biological material by bubbling N through the soln. at 90° C for 60 min. (average recovery, 101·9 ± 9·5 per cent.), or by distilling at + 20° C and 10 mm (Hg) for 5 min. (98 ± 14·6 per cent.), and was absorbed in the pyridine soln. at − 18° C. **I** can be estimated in the presence of trichloroacetic acid (**II**) by distillation under reduced pressure and determining it in aq. soln.; the average recovery is 107·5 ± 32·4 per cent. when ≃ 10 μg are present, and 77·5 ± 13·8 per cent. for ≃ 56 μg. **II** is determined in the residue with an average recovery of 89 ± 9·8 per cent. if the absolute amounts are 5 to 500 μg. In blood, **I** was determined in the presence of **II** with the same accuracy as in aq. soln., but **II** could be determined only to 60 per cent. In the air, **I** can be determined with an error of ± 20 per cent. in amounts < 10 μg and ± 5 per cent. in > 10 μg. Chem. Abstr.

3082. **A new method for peroxide determination.** S. Arrhenius (*Acta Chem. Scand.*, 1955, **9** [4], 715–717).—A method for the determination of peroxide is described and discussed. To 1 ml, or less, of an aqueous solution containing *tert.*-butyl hydroperoxide or di-*tert.*-butyl peroxide, 10 ml of a solution of 15·2 mg of vanillin (0·01 *M*) in 70 per cent. (by vol.) $H_2SO_4$ are added. After 20 hr. in a water bath at 37° C and dilution with 20 ml of ethanol, the extinction is measured in a Klett-Summerson photometer, filter 60 being used. At this dilution the method covers the concentration range $10^{-5}$ to $10^{-6}$ *M* (1 to 100 μg). O. M. Whitton

3083. **Determination of ethanol by the formation of ethylxanthate. A new volumetric method for the determination of ethylxanthate, and the stability of its solution.** Yoshijiro Arikawa and Takio Kato (*Technol. Rep. Tohoku Univ.*, 1954, **19** [1], 104–110).—See *Anal. Abstr.*, 1955, **2**, 2767. R. J. Magee

3084. **The determination of glyoxal and glyoxalic acid.** F. Salzer (*Z. anal. Chem.*, 1955, **146** [4], 260–273).—Total glyoxal and glyoxalic acid in the presence of other organic acids is determined by adding a known excess of semicarbazide hydrochloride, treating the excess with $HIO_3$ and titrating the liberated I with $Na_2S_2O_3$. Glyoxal is then determined alone by neutralising the acids with *N* NaOH, adding a known excess of *N* NaOH, allowing the reaction $(CHO)_2 + NaOH = CH_2OH{\cdot}COONa$ to take place, and finally titrating the excess of *N* NaOH. R. Stern

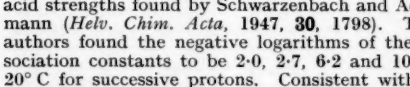
3085. **Paper-chromatographic analysis of acids—horizontal migration method. IV.** V. K. Mohan Rao (*J. Sci. Ind. Res., B, India*, 1955, **14** [4], 161–165).—The $R_F$ values of a number of organic acids and phenols, including volatile acids, have been determined by the modified Rutter technique of paper partition chromatography, using basic solvents. The procedure adopted was essentially as previously described (*Anal. Abstr.*, 1954, **1**, 2443. The $R_F$ values of aliphatic acids suggest that a clear separation of the lower members of the series is possible. G. C. Jones

3086. **Determination of methylimino groups. V. A new simplified apparatus.** F. Franzen and H. Pauli (*Mikrochim. Acta*, 1955, [4], 845–850).—The errors likely to arise from the apparatus and procedure commonly used for micro-determinations of alkylimino groups are discussed, and a new apparatus, obviating some of these errors and having a smaller internal vol., is described and illustrated. The main source of error in the older arrangements is the vertical distillation-tube, which conduces to the thermal decomposition of alkyl iodide when the temp. reaches 300° C. W. J. Baker

3087. **Brief note on the use of amalgams in the indirect micro-determination of ethylenediaminetetraacetic acid.** P. Wehber (*Mikrochim. Acta*, 1955, [4], 911).—The ions of some of those elements that are not adaptable to chelatometry can be reduced to definite valencies by means of a suitable liquid amalgam. In dil. acid soln., and with exclusion of oxygen from the amalgam (Zn, Cd or Bi), there can be obtained an equiv. amount of metal ions ($Zn^{++}$, $Cd^{++}$ or $Bi^{+++}$). These can be separated by reduction processes and then titrated with EDTA after removal of any interfering elements. A simple amalgam-reductor, in which reduction and titration can be effected, has been devised. W. J. Baker

3088. **Chelatometry. I. Volumetric micro-determination of EDTA using visual redox indicators.** P. Wehber (*Mikrochim. Acta*, 1955, [4], 812–820).—Within the pH range from 4 to 5, the titration of EDTA (disodium salt) (**I**) with 0·01 *M* aq. $FeCl_3$ in the presence of Variamine blue B (4-amino-4′-methoxydiphenylamine) as redox indicator yields a sharp end-point only if 2:2′-dipyridyl (0·25 per cent. in aq. $NH_3$) is present as auxiliary sequestrant for $Fe^{++}$. Several elements, *e.g.*, Al, can be determined indirectly by treating the soln. with excess of **I** and back-titrating with standard aq. $FeCl_3$ or other ferric salt. This procedure, which is discussed, can also be adapted to the simultaneous micro-determination of Fe and Al. To avoid any irreversible oxidation, the indicator should be added towards the end of the titration. W. J. Baker

3089. **The infra-red spectra of ethylenediaminetetra-acetic acid and its di- and tetra-sodium salts.** D. Chapman (*J. Chem. Soc.*, 1955, 1766–1769).—The infra-red spectra, between 650 and 3500 $cm^{-1}$, of solid EDTA (**I**) and its di- and tetra-sodium salts do not support the mode of ionisation previously suggested for **I** to account for the sequence of acid strengths found by Schwarzenbach and Ackermann (*Helv. Chim. Acta*, 1947, **30**, 1798). These authors found the negative logarithms of the dissociation constants to be 2·0, 2·7, 6·2 and 10·3 at 20° C for successive protons. Consistent with the characteristics of the infra-red spectra, the following mode of ionisation is suggested. The first and second protons are removed from opposite ends of the molecule, which then approximates to two dibasic acids. The disodium salt will then have the structure—



The third proton will be removed from between the carboxyl - carboxylate link, and $pK_3$ will therefore be higher than $pK_1$ or $pK_2$. The fourth proton will now tend to migrate to the nearby nitrogen atom so that $pK_4$ will be high, corresponding to the energy required to remove a proton from a nitrogen atom. K. A. PROCTOR

3090. **Mass-spectrometric analysis of high-molecular-weight saturated hydrocarbons.** R. J. Clerc, A. Hood and M. J. O'Neal, jun. (*Anal. Chem.*, 1955, **27** [6], 868–875).—Alkanes, non-condensed and condensed cyclo-alkanes, mono- and di-cyclic aromatics, as well as the relative abundance of *cyclo*pentyl and *cyclo*hexyl rings as free structures, are determined in high-boiling petroleum fractions by a mass-spectrometric method, after preliminary separation by chromatography into a saturate concentrate and one or more aromatic concentrates. The paper deals with a method of interpreting the mass spectra of the saturate fractions. Mono-aromatic and naphthalene components are also included. Pure compounds of a single hydrocarbon type are analysed with an accuracy of $\simeq$ 95 per cent. K. A. PROCTOR

3091. **The micro-photometric determination of phenol.** G. Gorbach, O. G. Koch and G. Dedic (*Mikrochim. Acta*, 1955, [4], 882–887).—In the micro-photometric procedure described, the phenol in 1 ml of sample soln. is determined by measuring the light transmission, in 10-cm capillary cells at 590 to 610 m$\mu$, of the blue dye produced when phenol reacts with 2:6-dibromoquinone-4-chlorimine at pH 9·4. Phenol contents of 0·01 to 5 $\mu$g per ml can be determined with an error of $\pm$ 2·5 per cent. W. J. BAKER

3092. **Quantitative estimation of phenol and o-cresol in mixtures.** M. Krahl (*Kunststoffe*, 1955, **45** [6], 224–225).—A method is described for estimating phenol (**I**) and *o*-cresol (**II**) in mixtures, which is based on the different reaction velocities with formaldehyde (**III**) in the presence of a strong mineral acid. The reaction velocity of **I** is four times that of **II**. In this method an aq. solution of the sample is mixed first with aq. **III**, and then with $H_2SO_4$, added as rapidly as possible from a pipette, and the time is noted for the development of a definite cloudiness. This stage is observed by a deflection on a meter, actuated by a selenium cell on to which a beam of light falls after traversing a 40-mm length of the solution. Analyses are described in which each 10 ml of an aq. soln. (2·5 per cent.) of sample is treated with 20 ml of an aq. soln. containing 400 ml per litre of 30 per cent. **III** and 600 ml per litre of 38 per cent. $H_2SO_4$, and graphs are given to show the clouding times of the resulting compositions for mixtures of **I** and **II** ranging from 0 to 100 per cent. of each component. Other concn. of sample solution are also shown to be useful, *e.g.*, 2·375 and 2·25 per cent. A dilution of 10 per cent. increases the clouding time by $\simeq$ 11 per cent. for **I** and 18 per cent. for **II**. Increasing the concn. of $H_2SO_4$ in the added solution (to 372·5 g per litre) decreases the clouding time (to approx. one-third). H. L. WHITEHEAD

3093. **Determination of phenol in salicylic acid.** E. von Schivizhoffen (*Z. anal. Chem.*, 1955, **145** [3], 184–187).—Phenol is coupled with diazotised *p*-nitroaniline in slightly acid soln. (pH 5·5 to 6), the resulting dye being extracted with benzene and determined colorimetrically. Coupling of salicylic acid takes place more slowly, but any resulting dye is removed by shaking the benzene extract of the mixture of the two dyes with $NaHCO_3$ soln. The phenolic dye is subsequently extracted with 0·2 *N* NaOH and determined colorimetrically in aqueous solution, the colour in benzene soln. being too weak. A calibration curve is provided. The method is suitable for 0·1 to 1·5 per cent. of phenol. P. HAAS

3094. **Chromatographic determination of small amounts of o-cresol in cresol mixtures.** H. Stoltenberg (*Z. anal. Chem.*, 1955, **146** [3], 181–190).—Couple mixed cresols containing a max. of 3 mg of *o*-cresol in aq. NaOH with an excess of diazotised *p*-nitroaniline. Acidify with $H_2SO_4$ and extract with chlorobenzene. Chromatograph on Brockmann's alumina, to which 4 per cent. of $H_2O$ is added. Separate the azo-dye zone of *o*-cresol with chlorobenzene as the eluting agent. Measure the extinction coefficient of the *o*-cresol azo dye, after purification on a second alumina column, with *iso*propanol as eluting agent. This procedure can be carried out in the presence of small quantities of phenol, xylenols and *o*-ethylphenol in addition to *m*- and *p*-cresols. Quantities $<$ 0·1 per cent. of *o*-cresol can be accurately determined. R. STERN

3095. **Identification of methylene ethers of o-dihydric phenols.** F. Feigl and L. Hainberger (*Mikrochim. Acta*, 1955, [4], 806–811).—The sensitive spot-test described is based on the heating of a cyclic methylene ether with conc. $H_2SO_4$ at 170° C, whereby formaldehyde vapour is evolved and can be identified by the violet coloration it gives when in contact with conc. $H_2SO_4$ containing chromotropic acid. The procedure, which is applicable to alkaloids, will reveal from 0·1 to 0·5 $\mu$g of a methylene ether. W. J. BAKER

3096. **The specific coloration of benzylamine-type compounds in the ninhydrin colour reaction. I.** Eiichi Takagi, Mitsuo Mangyo, Masanobu Sawai and Isao Ensaka (*Bull. Chem. Soc. Japan*, 1955, **28** [3], 213–216).—The coloration formed on the reaction between benzylamine-type compounds and ninhydrin can be used for detecting a number of aminocarboxylic and aminosulphonic acids, amines, etc.; the colours range from yellow to purple on paper-chromatographic strips. Alloxan gives similar colorations. *Procedure*—An aq. soln. (0·001 ml) containing 0·5 per cent. of the amine is employed,

with a unidimensional ascending technique and development with a *n*-butanol - acetic acid - water mixture (4:1:1) at 15° to 18° C. The initial coloration is formed by spraying the paper, after 3 to 4 hr. running, with a 0·2 per cent. ninhydrin soln. in *n*-butanol; the yellow colour is developed by heating, and ultimately changes to purple. Several compounds, *e.g.*, benzylaniline and *p*-dimethylaminobenzylamine, give no specific reactions. It is established that colour changes with ninhydrin reagent in paper chromatography are due to the moisture content of the air. G. R. WHALLEY

3097. **Colorimetric determination of small amounts of hydrazobenzene.** M.Večeřa and J. Petránek (*Chem. Listy*, 1954, **48** [9], 1351–1353).—A new method for the determination of small amounts of hydrazobenzene is based on its rearrangement to benzidine, coupling of the diazotised amine with N-1-naphthylethylenediamine (**I**) and the colorimetric determination of the blue reaction product. Under the optimum conditions of concn., $\simeq$ 0·2 mg of benzidine per 10 ml of soln., the extinction curve is practically a linear function of concn. *Procedure*—Dissolve a suitable quantity of hydrazobenzene (*e.g.*, 10 mg) in ethanol (20 ml), add conc. HCl (5 ml), and dilute the mixture to 200 ml after setting it aside at room temp. for 90 min. Diazotise an ice-cooled aliquot (10 ml) with 0·5 per cent. $NaNO_2$ soln. (5 ml), and 5 min. later add 2 per cent. sulphamic acid (4 ml), followed by 10 ml of a soln. of 0·272 g of the dihydrochloride of **I** in 250 ml of $H_2O$. Dilute the resulting soln. to 250 ml and measure the extinction after 90 min., a green VG2 filter being used. The determination is unaffected by the presence of a large excess of ZnO in the sample, provided sufficient HCl is added to maintain the acidity necessary for diazotisation. G. GLASER

3098. **The preparation and determination of tropinone.** G. Gál, I. Simonyi and G. Tokár (*Magyar Kém. Foly.*, 1955, **61** [3], 74–77).—A 1 per cent. aq. soln. of tropinone (tropan-3-one) hydrochloride (1 to 8 ml) was diluted with $H_2O$ to 30 ml and the pH was adjusted to 2 with *N* HCl, or to 6 with *N* NaOH. A filtered 1 per cent. aq. Reinecke salt soln. is added in 20 to 30 per cent. excess (the supernatant liquid should remain pink). One hr. after dilution to 50 ml with $H_2O$, the ppt. is filtered off, washed with a little $H_2O$ and 2 × 5 ml of 96 per cent. ethanol, and dried at 105° C for 30 min. The residue is weighed and has a m.p. of 180° to 182° C. The method is also suitable for the determination of tropan-3-one in crude reaction mixtures. A. G. PETO

3099. **Determination of nitrofuran derivatives.** I. Shibazaki and G. Terui (*J. Fermentation Technol., Japan*, 1954, **32**, 326–333).—Existing methods of determining 5-nitro-2-furfuraldehyde semicarbazone (**I**) and 5-nitro-2-furylacrylamide (**II**) by microbiological assay, colorimetry after addition of alkali, and polarography were studied for comparison in practical use, with special reference to application in food technology and microbiological investigation. In microbiological assay by the cup method, with *Bacillus subtilis* as the test organism, concn. as low as 5 μg of **I** per ml and 1 μg of **II** per ml could be determined. The results were greatly affected by substances that exerted synergetic or competitive action on the activities of **I** and **II**. Colorimetry, after addition of alkali, could be applied to 1 to 2 μg of **I** per ml in a few ml of sample, but for **II** the sensitivity was only one-tenth as much as that for **I**, and it was necessary to heat at 90° to 100° C for 2 to 5 min. for development of the red colour. The effect of interfering substances was significantly reduced by extracting the furan derivatives from samples by ethyl acetate. With polarography, 3 to 5 μg of **I** and **II** per ml were determined in a few ml of solution by using McIlvain's buffer soln. and 0·1 *N* KCl as supporting salt. With biological samples, extraction of the furan derivatives by organic solvents was necessary in order to exclude interfering substances. A combination of the colorimetric method and polarography was satisfactory for determining **I** and **II** in a sample containing both. CHEM. ABSTR.

3100. **Identification of frozen liquid samples with the X-ray diffractometer.** H. N. Smith and H. H. Heady (*Anal. Chem.*, 1955, **27** [6], 883–888).—By using a low-temperature adapter capable of reaching — 100° C, the X-ray diffractometer has been employed to identify components of frozen liquid samples. A Pliofilm cover prevents frost formation on the sample. Identifications are made by comparison of the X-ray charts of known frozen liquids and the powdered frozen sample. The technique has been applied to identifying and making percentage estimates of the components of the liquid shale-oil distillate fractions of high boiling point. K. A. PROCTOR

3101. **Determination of insoluble constituents in weathered bituminous surfacings.** H. H. Hahn and A. M. U. Larink (*Chem. & Ind.*, 1955, [25], 703–704).—In the indirect determination of insoluble residues in weathered binders, after solvent extraction, which depends on wet oxidation with hot chromic acid and weighing of the $CO_2$ formed, errors may arise owing to the passage of $H_2SO_4$ vapours through the reflux condenser and traps to the absorption tube. This was overcome by introducing a solid-medium trap consisting of a 100-mm × 8-mm tube filled with Pregl's lead oxide and maintained at the temp. of boiling Dekalin, followed by a $CaCl_2$ or $Mg(ClO_4)_2$ absorption tube, and then by the Sofnolite - $Mg(ClO_4)_2$ tube for $CO_2$ absorption. No liquid traps were used and dil. $H_2SO_4$ was used instead of HCl in the blank carbonate determination. S.C.I. ABSTR.

3102. **Chromatography of dyestuffs intermediates. II. Paper chromatography of naphtholsulphonic acids.** J. Latinák (*Chem. Listy*, 1954, **48** [9], 1354–1359).—Paper chromatography is suitable for the separation of naphtholsulphonic acids (**I**) and 1-naphthol-8-sulphonic acid sultones (**II**), and for the determination of their purity. Two solvent systems have been used, *n*-butanol - acetic acid - water (4:1:5), and *n*-butanol - pyridine - water (3:1:1), on Whatman No. 4 paper. The $R_F$ values of fifteen **I** and three **II** in each system are listed; their magnitude is influenced primarily by the number of sulphonic acid groups in the naphthalene nucleus, less by the relative positions of these and the hydroxyl groups. The spots are detected either by their fluorescence in u.v. light or by spraying with a soln. of *p*-nitrobenzenediazonium chloride. The detection of **II** must be preceded by spraying with 5 per cent. KOH soln. G. GLASER

3103. **Quantitative X-ray determination of amorphous phase in wood pulps as related to physical and chemical properties.** G. L. Clark and H. C. Terford (*Anal. Chem.*, 1955, **27** [6], 888–895).—An attempt has been made to correlate the texture and crystallinity of wood pulps from widely different sources

and the properties of paper sheets made from these pulps. The percentage of amorphous phase of cellulose appears to be an important variable and has been determined by X-ray diffraction. The technique involves quantitative calibration and scattering correction standards, and appears to be of sufficient sensitivity to distinguish differences in crystallinity. The results show that mechanical grinding decreases, and that bleaching increases, crystallinity; that pulp density increases with increasing crystalline contents up to $\simeq$ 70 per cent., beyond which the density remains constant; that the tensile strength of paper appears to be a function of the amorphous cellulose content of the pulp; and that there is no definite correlation between paper tear-strength and the crystallinity of the pulp from which it was made. K. A. PROCTOR

3104. **Infra-red spectra of gels of metal soaps in organic liquids.** L. Robert and J. Favre (*Mikrochim. Acta*, 1955, [2–3], 517–524).—Infra-red spectrometry is applied to complex products such as firm greases, making use of additional information on the nature of the base oils, thickening agents and, for metal soaps, the type of fatty acids and metals present. The increase in at. wt., *e.g.*, from Li to Pb, is accompanied by a corresponding decrease in the fundamental frequency of the C:O group ($< 77$ cm$^{-1}$) and thus the metal in a soap can be characterised. D. R. GLASSON

3105. **The identification of colouring materials in cosmetic products by paper chromatography.** J. Deshusses and P. Desbaumes (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [2], 193–199).—The following three solvents have been found suitable for the identification, by paper chromatography, of colouring materials extracted from tooth pastes, mouth washes and other lotions: 96 per cent. ethanol, $H_2O$ and 25 per cent. aq. $NH_3$ (40 + 56 + 4); aq. $NH_3$ (2 per cent.) saturated with *iso*butyl methyl ketone; and acetone, $H_2O$ and conc. HCl (10 + 40 + 1). Lists of $R_F$ values, with the second and third solvents, for various colouring materials are given. Methods of extracting the materials are discussed. W. H. PARR

3106. **Analysis of fluorinated polyphenyls by mass spectrometer.** P. Bradt and F. L. Mohler (*Anal. Chem.*, 1955, **27** [6], 875–877).—A mass-spectrometric method has been used to investigate the mol. wt. and chemical composition of some fluorinated polyphenyls. The polymers are evaporated from a tube furnace directly into the ionisation chamber and the mass spectra are recorded as the furnace temp. is increased step by step. As molecule ions are predominant in the spectra, the interpretation of the results in terms of mol. wt. distribution is simplified. No difficulties, apart from the limitations of resolving power and mass measurement in an instrument designed for mol. wt. less than 350, were encountered in extending the mass range above 1700. K. A. PROCTOR

3107. **Note on leather analysis.** G. Forsyth (*J. Soc. Leath. Tr. Chem.*, 1955, **39** [4], 105–107).—The American and most of the European leather chemists' Societies recommend the grinding of samples for analysis in a Wiley mill; in the U.K., shavings are used. Results obtained from the analysis of samples from the same leather by both methods show little variation in moisture content, but extraction of water-solubles gives up to 5 per cent. variation unless the extraction is carried out at 20° C, when the two methods of sample preparation give comparable results. B. R. HAZEL

3108. **Specifications for reagents and equipment [for leather analysis].** American Leather Chemists' Association (*J. Amer. Leath. Chem. Ass.*, 1955, **50** [4], 173–177).—Detailed specifications are given of chemicals and equipment to be used in analyses according to the Official Methods of the Association —for the desiccants $H_2SO_4$, $P_2O_5$, $CaSO_4$, $Ba(ClO_4)_2$ and $Mg(ClO_4)_2$, for light petroleum, and for thermometers used in the analysis of oils, greases and their products. B. R. HAZEL

3109. **Estimation of chlorides and sulphates in leather.** J. Jany (*J. Amer. Leath. Chem. Ass.*, 1955, **50** [5], 235–238).—Inaccuracies of existing methods are discussed. In the proposed method finely ground leather is wetted, 10 per cent. $Na_2CO_3$ soln. is added, and the mixture is heated electrically, diluted, evaporated to dryness, and ashed completely at 400° to 450° C. The ash is dissolved in water, acetic acid is added, and the soln. is filtered. The filtrate is titrated against 0·1 *N* $AgNO_3$, with $K_2CrO_4$ as indicator, to determine Cl′, and $SO_4''$ is determined gravimetrically by pptn. with $BaCl_2$. In this method of ashing, interfering org. matter is destroyed completely. B. R. HAZEL

3110. **Resistance of leather to the growth of fungi.** American Leather Chemists' Association (*J. Amer. Leath. Chem. Ass.*, 1955, **50** [4], 177–179).—The resistance of leather, treated with a fungicide, to fungal spores is tested by dusting damp samples with a spore - sand mixture, and incubating them at 29° ± 2° C at R.H. > 85 per cent. for 30 days. Fungal resistance is estimated by visual comparison with a control sample of the same tannage but not treated with fungicide. B. R. HAZEL

3111. **The use of adsorption columns in the analysis of oil-in-water emulsions.** T. Green, R. P. Harker and F. O. Howitt (*Analyst*, 1955, **80**, 470–475).—By the general method described, the constituents of emulsions stabilised by different types of detergents are adsorbed on an ion-exchange resin and subsequently eluted. The resins are regenerated by the Permutit procedure, *e.g.*, Zeo-Karb is regenerated by percolation of HCl, followed by thorough washing with water and Soxhlet extraction with the solvent to be used for elution. The columns are made with an aq. slurry of the resin and provision is made for the application of pressure when required. A. O. JONES

See also Abstracts 2947, 3242, 3243, 3245, 3249, 3250.

## 4.—BIOCHEMISTRY

### INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

### Blood, Bile, Urine, etc.

3112. **Ultra-micro procedures in clinical chemistry.** W. T. Caraway and H. Fanger (*Amer. J. Clin. Path.*, 1955, **25** [3], 317–331).—Methods for determining glucose, urea N, creatinine, total protein, albumin, Na, K and Ca, chloride, $CO_2$-combining power, inorganic P, icterus index, bilirubin, cholesterol, thymol turbidity, cephalin flocculation, alkaline phosphatase, and amylase in blood are described. Most of the methods require only 0·01 ml of serum for a single determination. The results by these methods are in agreement with standard accepted macro procedures. R. S. TONKS

3113. **Turbidimetric method of fibrinogen assay.** A. H. Fowell (*Amer. J. Clin. Path.*, 1955, **25** [3], 340–342).—The method consists in measuring the turbidity of a suspension of salt-precipitated fibrinogen with a Coleman Junior spectrophotometer (Model 6A). Sodium citrate is used as anticoagulant and $(NH_4)_2SO_4$ reagent as the salting-out soln. R. S. TONKS

3114. **A tablet test for blood in urine.** E. J. Watson-Williams (*Brit. Med. J.*, 1955, 1511–1513).—Tablets are prepared so that each contains 50 mg of citric acid, 35 mg of barium peroxide, 12·5 mg of o-tolidine and 2·5 mg of $Na_2CO_3$. These tablets retain their sensitivity for at least a year, if kept in a tightly stoppered container. Place one drop of urine on a 2·5-cm square of Whatman No. 1 filter-paper and allow it to spread; place a tablet in the centre of the paper and allow two drops of tap-water to flow over it. A blue ring developing around the tablet within 2 min. indicates that a significant amount of haemoglobin ($< 150$ μg in 100 ml of urine) is present. The sensitivity of the test is not significantly influenced by pH or temp. H. F. W. KIRKPATRICK

3115. **Plasma prothrombin time.** M. C. Rhees, L. D. Ellerbrook and D. V. Brown (*Amer. J. Clin. Path.*, 1955, **25** [4], 453–459).—The method involves careful control of the temperature of the reacting mixture at 36° to 37° C, a minimum of agitation during the test, and photo-electric detection of the instant of clotting. This procedure results in greater precision and shorter, more accurate one-stage plasma prothrombin times. R. S. TONKS

3116. **The caramel test of cerebrospinal fluid.** A. Sole (*Dtsch. med. Wochschr.*, 1955, **80** [22], 869).—The following simple test is suggested for the determination of glucose in cerebrospinal fluid. The sample (3 to 5 ml) is heated in an autoclave for 1 hr. at 1½ atm. pressure. Under these conditions glucose is converted into caramel, and it is claimed that the concn. is proportional to the colour. The lower limit of detection appears to be 40 mg per 100 ml. G. W. CAMBRIDGE

3117. **The action of electrolytes and methanol in increasing emission in flame-photometric determination of potassium.** H. Siebert and S. Rapoport (*Biochem. Z.*, 1955, **326** [6], 413–419).—The action of Na, Ca, Ba, Sr, Li and methanol on the flame-photometric estimation of K has been studied. Sodium and methanol increase the emission. Some observations on the error involved in the determination of K in mixtures of Na and K are reported. The use of 20 per cent. methanol added to serum in estimations of K is satisfactory, as the increased emission is obtained with minimal protein precipitation. G. W. CAMBRIDGE

3118. **The determination of calcium in biological material.** W. H. Horner (*J. Lab. Clin. Med.*, 1955, **45** [6], 951–957).—The EDTA method is adapted for the photometric determination of Ca in serum, urine, faeces and diets. Ammonium purpurate (murexide) is incorporated as indicator in both test and EDTA-titrating soln., and optical density at 620 mμ is plotted after the addition of 1-ml increments of titrant, both before and after max. optical density is reached. The intersection of the extrapolated linear portions of the graph gives the end-point. Details are given for the construction of the titration assembly incorporating a 1-ml automatic pipette and intermittent air-agitation of the titrated soln. Materials with a high phosphate content are treated before assay with sodium tungstate and morpholine nitrate - $HNO_3$ reagents. Neither $Mg^{++}$ $< 100$ mg nor $Fe^{+++} < 10$ mg per 100 ml interfere and the method gives results that agree well with those obtained by a standard $KMnO_4$ - oxalate procedure. W. H. C. SHAW

3119. **Micro-determination of bromide in body fluids.** G. Hunter (*Biochem. J.*, 1955, **60** [2], 261–264).—Details are given for the application of the method of Hunter and Goldspink (*Anal. Abstr.*, 1954, **1**, 981) to the determination of $Br'$ in serum, cerebrospinal fluid, blood, urine, plasma and erythrocytes. The material should contain $> 100$ and preferably $< 25$ μg of Br; 1 μg of Br suffices. The method is based on the quant. conversion of $Br'$ into $BrO_3'$ by NaOCl; the Br is then liberated quant. and is converted into tetrabromorosaniline, which is determined colorimetrically. The org. matter in blood is destroyed giving a negligible residue of carbon if the dried blood is ignited at 600° C for 30 min. The method is unsatisfactory for volatile compounds and it has not been adequately tested for non-volatile org.-bound Br. The method, which may be useful for the determination of Br in plant and animal tissues, is 100 times more sensitive than the earlier titration method of Hunter (*Brit. Abstr. C*, 1953, 263). The standard deviation is $< \pm 5$ per cent. and the extreme range of variation is $< 10$ per cent. of the mean value. A batch of 12 to 18 determinations can be carried out in a few hours. J. N. ASHLEY

3120. **Determination of iodine in difficultly solubilised (dried) biological materials.** W. Oelschläger (*Z. anal. Chem.*, 1955, **146** [1], 11–17).—The available methods for the destruction of organic matter for the subsequent determination of I are critically reviewed. The method of Wilmanns (*Biochem. Z.*, 1937, **289**, 41) was found to be suitable for liquid biological materials. With difficultly solubilised biological materials, oxidise by the carefully controlled addition of $CrO_3$ and conc. $H_2SO_4$ under a reflux condenser. Heat with occasional shaking on a boiling-water bath for 4 to 6 hr., then boil under reflux for 20 to 30 min., then without refluxing till dense white fumes are evolved. The iodate formed is reduced with arsenite to iodine, which is distilled off in a special apparatus (illustrated) with steam and $CO_2$ into $K_2CO_3$. The iodine is determined either by titration by Winkler's method or colorimetrically. The method for the determination of iodine in hay is given in detail. R. STERN

3121. **The colorimetric determination of silicon in the micro-analysis of biological material and mineral dusts.** E. J. King, B. D. Stacey, P. F. Holt, D. E. Yates and D. Pickles (*Analyst*, 1955, **80**, 441–453).—The basic ferric acetate pptn. procedure for removing $PO_4'''$ from solutions intended for the determination of Si is critically examined. The new procedure described for the determination of Si in biological material without preliminary separation of $PO_4'''$ is based on the fact that, of the complexes formed by $PO_4'''$ and $SiO_2$ with molybdate in weak acid, only the molybdosilicate is reduced in strong acid. The reducing soln. (**I**) used is a 0·2 per cent. soln. of 1-amino-2-naphthol-4-sulphonic acid in an aq. soln. of 2·4 per cent. of $Na_2SO_3.7H_2O$ and 12 per cent. of $Na_2S_2O_5$. The method is applicable with acceptable accuracy to amounts of mineral dusts containing $\simeq 5$ mg of $SiO_2$. The sample is fused with $Na_2CO_3$, the melt is leached with water, the

soln. is treated with 19 ml of 10 *N* $H_2SO_4$, the vol. is adjusted to 250 ml and an aliquot (≡ 0·05 mg of $SiO_2$) is treated as already described.
A. O. JONES

3122. **Identification of urinary sugar.** F. W. Fales (*Amer. J. Clin. Path.*, 1955, **25** [3], 336–339).—A method for identifying urinary sugars by a fermentation test and simple paper chromatography is presented which is readily adaptable to the clinical laboratory.
R. S. TONKS

3123. **Estimation of monosaccharides by the orcinol - sulphuric acid reaction.** J. Brückner (*Biochem. J.*, 1955, **60** [2], 200–205).—A standard procedure is given for the characterisation and determination of individual monosaccharides in solution, singly or in binary mixtures. *Procedure*—Mix the carbohydrate solution (1·0 ml) and orcinol reagent [orcinol (0·4 g) in water (10 ml)] (1·0 ml) in a round-bottomed 100-ml flask. Cool in water and add, dropwise, 31·2 *N* $H_2SO_4$ (8 ml), while steadily rotating in cold water. This requires approx. 1·5 min. and heating of the mixture is avoided. Transfer part of the mixture (5 to 6 ml) to test-tubes (approx. 17 cm × 0·7 cm; glass thickness approx. 0·5 to 0·6 mm), which are covered with small glass marbles, and immediately immerse in boiling water for exactly 50 sec. Cool immediately in cold water for 3 min. and measure the colour spectrophotometrically or colorimetrically; the amount of carbohydrate is then ascertained from calibration graphs.
J. N. ASHLEY

3124. **New micro-method for determination of glucose.** L. Panizo Alonzo and J. Martínez Bruna (*Laboratorio, Granada*, 1953, **15**, 301–317; 401–422).—The method is based on the colour reaction of thymol with the furfuraldehyde derivative produced by the action of $H_2SO_4$ on glucose. The sample is deproteinised by $Cd(OH)_2$, according to the method of Fujita and Iwataka (*Chem. Abstr.*, 1932, **26**, 1313), acidified with $H_2SO_4$ and treated with alcoholic thymol. The red colour is compared with that of previously prepared standard soln. The results are highly accurate, even with quantities of sample as small as 0·05 ml. The method is applicable to most types of body fluids, avoids the too high results given by reduction - oxidation methods in tests of diabetics, allows determination of other sugars in diabetic blood when employed with reduction - oxidation tests, and may be useful for the more extensive study of the metabolism of sugars.
CHEM. ABSTR.

3125. **Some observations on the determination of fructose [in biological systems] by the Seliwanoff reaction.** W. Chefurka (*Analyst*, 1955, **80**, 485–486).—To overcome the deviations from Beer's law that the Seliwanoff reaction for fructose exhibits, it has been recommended that at least three working standards should be used. It is now found that the need for three standards can be eliminated by using a calibration graph that obeys Beer's law provided sufficient time is allowed for max. colour development. The stability of the colour with time was investigated by following the procedure of Roe (*Brit. Abstr. A*, 1934, 1379). The determinations were made at 514 mμ, the absorption max. of the coloured complex. The components were heated in a test-tube for exactly 8 min., cooled and the colour intensity was measured subsequently at various intervals. The plotted results show that the time required for max. intensity of colour depends on the concn. of fructose. At 200 μg per ml, the max. is attained at ≃ 3 hr. after cessation of heating and is stable for 1 hr. Even at 50 μg of fructose per ml, ≃ 1 hr. is required. Probably no serious error would be encountered at 20 μg per ml, for at this concn. max. colour depth is attained very quickly. Thus, provided enough time is allowed for colour development, a calibration graph obeying Beer's law can be obtained up to a concn. of 200 μg per ml. The slope of the graph is influenced by the concn. of the resorcinol soln.; a concn. > 0·1 per cent. w/v decreases the sensitivity of the reaction.
A. O. JONES

3126. **Enzymic estimation of L(+)-lactic acid with lactic acid dehydrogenase.** G. Pfleiderer and K. Dose (*Biochem. Z.*, 1955, **326** [6], 436–441).—The following method can be applied to the determination of lactic acid in concn. of 3 to 35 μg per ml. If blood is used, the proteins must be removed by preliminary treatment. Blood (5 ml) is treated with $HClO_4$ (6 per cent.) (5 ml) and centrifuged. A portion of the supernatant fluid (5 ml) is treated with 2 *N* KOH until neutral, and made up to 10 ml with $H_2O$. The quantities used in the test are: test soln. or standard lactic acid soln., 0·01 to 0·12 ml; diphosphopyridine nucleotide (DPN) 0·2 ml, equiv. to $1·68 \times 10^{-2}$ millimoles of pure DPN per ml; $Na_2CO_3$ - $NaHCO_3$ buffer (pH 9·7) 3·19 to 3·08 ml; lactic dehydrogenase (150 μg per ml) 0·1 ml. The initial extinction $E_0$ is measured at 340 mμ before the addition of the lactic dehydrogenase and $E_1$ at 5 minutes after the start of the reaction; $E_1 - E_0$ thus depends on the concn. of lactic acid. The error is given as ± 3·5 to 4·0 per cent.
G. W. CAMBRIDGE

3127. **The colorimetric determination of lactic acid in sub-microgram quantities.** S. L. Bonting (*Arch. Biochem. Biophys.*, 1955, **56** [2], 307–317).—The method of Barker and Summerson (*J. Biol. Chem.*, 1941, **138**, 535) is adapted for the determination of 0·25 to 0·025 μg of lactic acid in 25-μl samples, and has a standard deviation of ± 0·0051 μg. Preliminary treatment of samples with $CuSO_4$ - $Ca(OH)_2$ is recommended for deproteinisation and for the partial or complete removal of some interfering substances. The precautions necessary to prevent contamination with extraneous lactic acid are discussed and a detailed statistical examination of each step in the procedure is made.
W. H. C. SHAW

3128. **A modified method for the micro-determination of citric acid.** B. McArdle (*Biochem. J.*, 1955, **60** [4], 647–649).—A modification of the colorimetric method of Taylor (*Brit. Abstr. C*, 1953, 281) is described for the determination of 10 to 80 μg of citrate in biological fluids. Greater sensitivity and accuracy are attained by increasing the concn. of $H_2SO_4$ to 16·5 *N* before the addition of bromide - bromate - vanadate to form pentabromoacetone, and by the use of a solution containing thiourea (4), borax (2) and $Na_2S$ (0·2 per cent.) instead of 2 per cent. $Na_2S$ soln. for development of the final colour. Very high concn. of glucose interfere slightly; salicylic acid and other aromatic substances should be removed by a preliminary bromination.
J. N. ASHLEY

3129. **The micro-analytical determination of citric acid in biological substrates.** K. Täufel, R. Pohloudek-Fabini and U. Behnke (*Z. anal. Chem.*, 1955, **146** [4], 244–250).—The papers presented during the last 25 years on the micro-analytical determination of citric acid are critically reviewed, and a method is

described for the conversion of citric acid into pentabromoacetone and photometric determination of the yellow colour produced by this with $Na_2S$. The main sources of error are traced to non-purification of the light petroleum (40° to 70° C) used for extraction, and age and purity of the stock $Na_2S$ soln. A margin of error of approx. $\pm$ 3 $\mu$g was found for the whole range (10 to 100 $\mu$g). This was not increased by the presence of other organic acids. R. STERN

3130. **The accuracy of the determination of pyruvic acid as 2 : 4-dinitrophenylhydrazone.** Von S. Markees (*Experientia*, 1955, **11** [5], 205–208).—The accuracy of the direct colorimetric estimation of pyruvic acid in blood has been checked by a quant. chromatographic method. To do this a new procedure for the quant. chromatography was elaborated to avoid considerable losses due to the sensitivity of the 2:4-dinitrophenylhydrazone of pyruvic acid to light, temperature, solvents or acids. Nevertheless a difference of about 20 per cent. still remained between the two procedures, which could be explained by the formation of two isomers of the hydrazone, in addition to a smaller purely technical loss. This difference could be corrected by estimating the yield of hydrazone from known quantities of pyruvate. The direct colorimetric estimation of pyruvic acid as 2:4-dinitrophenylhydrazone is sufficiently specific; it includes no appreciable quantities of other keto acids and furnishes reliable values. R. S. TONKS

3131. **An enzymic estimation of L-aspartic acid.** G. Pfleiderer, W. Gruber and T. Wieland (*Biochem. Z.*, 1955, **326** [6], 446–450).—The estimation of aspartic acid is based on its transamination in the presence of oxoglutarate and a suitable enzyme system to oxalo-acetic acid. In the presence of malic dehydrogenase and reduced diphosphopyridine nucleotide (DPNH) this is converted into malic acid, and the decrease in DPNH concn. is observed at 366 m$\mu$. The following quantities are used: test soln. or neutral soln. of aspartic acid, 10 to 120 $\mu$g (0·1 ml); DPNH soln., $9 \times 10^{-7}$ moles (0·1 ml); malic acid dehydrogenase, 17·8 mg of protein per ml, 1600 units per mg (0·02 ml); aspartic - oxaloacetic transaminase, 60 mg of protein per ml, 16 units per mg (0·03 ml); 0·03 *M* phosphate buffer (pH 7·4), 1·7 ml; and 0·1 *M* oxoglutaric acid soln., 0·05 ml. A zero reading is determined at 366 m$\mu$ before the addition of oxoglutarate. The reaction is complete in 10 min. Graphs are given to show the relationship between the amount of aspartic acid and the decrease in DPNH concentration. G. W. CAMBRIDGE

3132. **Determination of free non-volatile fatty acids [in plasma].** J. van der Vies (*Biochem. J.*, 1955, **60** [4], 671).—A simple method is described for the determination of free fatty acids in normal and lipaemic plasma. *Procedure*—Add the plasma (2 ml), containing either heparin or Na citrate as anticoagulant, to aq. $HPO_3$ [6 ml; prepared from $HPO_3$ (50 g), NaCl (250 g) and water to 1 litre] in a flask (100 ml). After a few min., add ethanol (16 ml) containing 0·4 per cent. of pentanol, and then add distilled light petroleum (boiling range 40° to 60° C; 20 ml). Insert the stopper and shake by hand for 1 min., then filter the upper layer through a dry paper, taking care to minimise evaporation. Evaporate the extract (10 ml) and dry the residue *in vacuo*. Add neutralised ethanol (5 ml) containing thymol blue (0·6 mg per 100 ml) and gently reflux for 3 min., then titrate, under N, with 0·01 *N* NaOH. A control is carried out with water (2 ml) instead of plasma. The differences between duplicate determinations have a standard deviation of $\pm$ 0·14 micro-equiv. J. N. ASHLEY

3133. **A method of determining esterified fatty acids and its application to blood serum.** M. Jarrier and J. Polonovski (*Bull. Soc. Chim. Biol.*, 1955, **37** [4], 495–499).—The method is a modification of one described by Bauer and Hirsch (*Brit. Abstr. C*, 1949, 294), the ether recommended being replaced by ethanol. Four reagents are required. (*A*) Hydroxylamine hydrochloride soln., 2·5 per cent. in 95 per cent. ethanol. (*B*) NaOH soln., 2·5 per cent. in 95 per cent. ethanol. Both these soln. must be kept in a refrigerator. (*C*) Stock soln. of ferric perchlorate. For this, 0·4 g of iron or 1·16 g of $FeCl_3$ are heated with 20 ml of water, 3 ml of $HNO_3$ and 15 ml of $HClO_4$ until fumes are evolved. When cool, the liquid is poured into a 100-ml calibrated flask, to which are added 40 ml of water, 10 ml of $HNO_3$, and $HClO_4$ to make up to the mark. (*D*) A soln. of ferric perchlorate is prepared by diluting 5 ml of *C* with 95 per cent. ethanol to 100 ml. This should be done 5 min. before use, as the soln. is unstable. The sample of lipids to be analysed is treated in the way exemplified with ethyl palmitate. The material (284 mg) is dissolved in 100 ml of ether and 5 ml of this are diluted to 50 ml. Of this soln., increasing quantities of 1 to 6 ml or 1 to 6 micro-equiv. are put into six test-tubes and evaporated to dryness *in vacuo*. Each residue is dissolved in 0·3 ml of reagent *A* and 0·3 ml of reagent *B* is added. After 1 hr., during which time the formation of the hydroxamate is completed, 10 ml of reagent *D* are added and the tubes are then heated at 25° C for 20 min. The extinction coefficients are then measured at 250 m$\mu$ with a Unicam spectrophotometer, and a calibration curve is constructed by plotting optical density against micro-equivalents; points lie on a straight line. The linear curve prepared in this way from ovolecithin gave results that agreed closely with the calculated values. A cerebroside extracted from a sheep's brain and treated in the same way gave no colour with the reagents; this was as expected, since it contained only free acids, which give no colour, the reaction being given exclusively by esterified fatty acids, which alone form the hydroxamates, according to the equation—

$$R{\cdot}COOR' + NH_2{\cdot}OH = R'{\cdot}OH + R{\cdot}CO{\cdot}NH{\cdot}OH,$$

and later combine with the ferric salt to give a reddish-violet colour. P. HAAS

3134. **Separation of small quantities of saturated higher fatty acids by reversed-phase paper chromatography.** B. D. Ashley and U. Westphal (*Arch. Biochem. Biophys.*, 1955, **56** [1], 1–10).—In the methods described, 10 to 50 $\mu$g of saturated fatty acids ($C_{12}$ to $C_{24}$) are separated on filter-paper impregnated with liquid paraffin or with rubber latex. Details are given for preparing the paper and for both ascending and descending chromatography in jars, and for the ascending technique in test-tubes. On paraffin-treated paper, the chromatograms are developed with 85, 90 or 95 per cent. aq. methanol (for $C_{12}$ to $C_{16}$, $C_{14}$ to $C_{20}$ and $C_{18}$ to $C_{24}$ fatty acids, respectively) containing 0·001 *N* HCl. Development on latex-treated paper is with 80 per cent. aq. methanol containing 0·001 *N* HCl and saturated with *cyclo*hexane or trimethylpentane. The fatty acid spots are detected with bromothymol blue or, more sensitively, by treatment with Pb acetate followed by $H_2S$ or K rhodizonate. W. H. C. SHAW

3135. **Column partition chromatography of the fatty hydroxamic acids.** J. B. Davenport (*Chem. & Ind.*, 1955, [25], 705–706).—The use was studied of the hydroxamic acids as solid derivatives for the characterisation of naturally occurring fatty acids and to separate mixtures of them. The hydroxamic acids were prepared by treatment of the methyl esters with an alkaline solution of $NH_2OH$ at room temp. After acidification and dilution, the saturated acids were filtered off, whilst the unsaturated derivatives were extracted with ether. Satisfactory chromatographic separations were achieved with columns of cellulose .powder and a solvent system of methanol, "hexane" (4·5 per cent. aromatics, boiling range 65° to 75° C), water and acetic acid (50:50:5:1, by vol.). Some successful separations are tabulated. S. C. I. ABSTR.

3136. **Paper-chromatographic method of estimating free histamine in the blood of normal and hypertensive persons.** E. P. Stepanyan (*Klin. Med., U.S.S.R.*, 1954, **32** [7], 42–46).—A 5-ml sample of oxalated blood containing 0·0002 per cent. of semicarbazide, an antihistaminase, is diluted with an equal amount of twice-distilled $H_2O$ in a glass-stoppered test-tube, and 3 g of a mixture of anhyd. $Na_2SO_4$ and $Na_3PO_4$ (1:6·25) are added, followed by 5 ml of butanol. After 3 min. the mixture is shaken vigorously to disperse the albuminous ppt. The test-tube is then shaken in a shaking machine for 45 min., centrifuged for 15 min., and the butanol layer is transferred to another glass-stoppered test-tube containing 1 ml of 0·5 *N* $H_2SO_4$. The shaking is repeated for 45 min., the centrifuging for 5 min., and the alcoholic layer is removed; 3 g of the sulphate - phosphate mixture and 3 ml of butanol are added, and the product is shaken and centrifuged for 45 and 5 min., respectively. Both alcoholic layers are concentrated in a porcelain dish to a very small volume, the sides of the dish are rinsed with butanol, and the vol. is reduced to between 0·1 and 0·05 ml. The cooled soln. is dropped by micro-pipette on to Whatman No. 1 filter-paper, which is warmed. The same paper is treated with several dilutions of a standard soln. of histamine and placed in a small jar three-quarters filled with ammonia-saturated butanol (**I**). The jar is placed inside another vessel containing a Petri dish filled with **I**, then this outer vessel is tightly covered and incubated at 18° to 20° C for 15 to 17 hr. When taken out, the paper is dried at 100° C for 2 hr., allowed to cool and, after 30 min., is sprayed with a diazo mixture [prepared by cooling 10 ml of *p*-nitroaniline soln. (0·1 per cent. in HCl) on ice for 1 hr., adding 1 ml of 4 per cent. $NaNO_2$ soln. dropwise and stirring; the mixture must be colourless]. The paper is then sprayed with 10 per cent. $Na_2CO_3$ soln. and warmed for 5 to 7 min. to develop the red colour resulting from the interaction of histamine and the diazo mixture. The amount of histamine can be determined by comparing the intensity and size of the stain with those from the standard soln. Normal values found with this method (5 to 7 $\mu$g per 100 ml) agree closely with those obtained through biological assay. In the first stage of hypertension the histamine blood level was 7 to 10 $\mu$g, in the second stage 30 to 50 $\mu$g, mean value 21·6, and in the third stage (sclerotic) 2 to 10 $\mu$g, mean value 7. CHEM. ABSTR.

3137. **A rapid technique for estimating benzidines [in urine] in industrial exposure. An application to benzidine and some of its 3:3′-disubstituted analogues in urine.** L. J. Sciarine and (the late) J. A. Mahew (*Arch. Ind. Hlth*, 1955, **11** [5], 420–421).—A rapid colorimetric method for the determination of benzidine and 3:3′-disubstituted analogues by using chloramine T is described. The method is particularly useful for the determination of benzidine in urine. Benzidine compounds substituted in the position *meta* to the amino group do not react to the same extent as the *o*-substituted compounds, because of the increased stability conferred by the substituents in these positions. The accuracy in the 2 to 10-$\mu$g range is $\pm$ 10 per cent., while that for less than 2 $\mu$g is approximately $\pm$ 15 per cent. The accuracy for the determination of dichlorobenzidine, *o*-tolidine and dianisidine is similar to that for benzidine. I. JONES

3138. **The quantitative determination of some products of metabolism of amidopyrine in urine.** W. Hennig and H. Weiler (*Arzneimittel-Forsch.*, 1955, **5** [2], 60–61).—A method is described for the separate colorimetric determination of rubazonic acid (**I**), 4-aminophenazone (**II**) and 4-acetamidophenazone (**III**) in urine. **I** is first separated from **II** and **III** by adsorption on to an alumina column. Elution with ethanolic ammonia gives a violet solution. The colour intensity is measured with an S55 filter. The accuracy of the determination is $\pm$ 3 per cent. **II** is determined in the **I**-free urine by oxidation with potassium ferricyanide in the presence of phenol to give a red dye, which is extracted with $CHCl_3$. The colour intensity of the organic phase is measured with an S49 filter. The accuracy is $\pm$ 4 per cent. **III** gives the same reaction as **II** after preliminary hydrolysis by refluxing with sulphuric acid. A. R. ROGERS

3139. **The colorimetric determination of amidopyrine in serum.** R. Haslinger and W. Strunz (*Arzneimittel-Forsch.*, 1955, **5** [2], 61–62).—Errors may arise in the determination of amidopyrine in serum according to the method of Pulver (*Brit. Abstr. C*, 1950, 239) owing to interference by the breakdown product 4-aminophenazone. These may be eliminated by preliminary acetylation of the sample; 4-acetamidophenazone gives a negative reaction. A. R. ROGERS

3140. **Determination of acetylaminobenzaldehyde thiosemicarbazone (thiacetazone) in plasma. A sensitive and simple technique applicable to examinations in series.** M. C. Jardin and J. Rayroux (*Ann. Pharm. Franç.*, 1955, **13** [3], 186–192).—Published methods for the determination of thiacetazone (**I**) by hydrolysis and diazotisation and coupling of the free $NH_2$ group are not satisfactory for application to the plasma of lepers undergoing treatment, owing to the low concn. ($\simeq$ 5 mg per litre). A method is developed which minimises losses and depends on the visual comparison of the product of coupling with Tréfouël reagent IV (naphthyldiethylpropylenediamine) (**II**) for the test and standard samples after extraction in *iso*-amyl alcohol. *Procedure*—Citrated blood (10 ml) is sedimented for a few hours, and to 2 ml of the plasma are added 5 ml of *N* HCl and (after 5 min.) 5 ml of water. Similar mixtures of standards are prepared (preferably also in plasma) from a standard solution of **I**. The products are hydrolysed for 45 min. on a bath of boiling water, preferably with agitation. After being cooled, the liquid is transferred to a calibrated test-tube and made up to 12 ml. To each tube are added 8 ml of 15 per cent. trichloroacetic acid (7·5 per cent. for standards in water), and after shaking and waiting for 2 min. the

solution is filtered. The filtrate (15 ml) is cooled in ice and 1 ml of 0·1 per cent. $NaNO_2$ is added. After 5 min., 1 ml of 1·5 per cent. ammonium sulphamate and, after another 3 min., 1 ml of 0·1 per cent. **II**, are added, with shaking. The tubes are left in the dark for 10 min. and 1·7 ml of *iso*amyl alcohol are added. After addition of 0·3 ml of methanol to break the emulsion the colours of the test solutions are compared with the standards. For higher concn. a spectrophotometer may be used.

E. J. H. BIRCH

3141. **Determination of poly(vinylpyrrolidone) (PVP) in water and in plasma.** C. Discombe and H. B. W. Creig (*Ann. Biol. Clin.*, 1954, **12**, 415–418).—The method is based on the colour given by PVP in the presence of iodine and $ZnSO_4$. The reagent contains 5 g of $ZnSO_4$ and 10 ml of 0·1 *N* iodine in 0·2 *N* KI soln. made up to 100 ml. For aq. soln., 1 ml of the reagent is added to 10 ml of a soln. containing $\geqslant$ 0·11 mg of PVP, and the colour is read at 432 mμ against a reagent blank. For plasma, 0·5 ml of 0·6-satd. $CuSO_4$ soln. and 0·5 ml of 0·6-satd. $K_4Fe(CN)_6$ soln. are added to 8 ml of plasma, and the mixture is centrifuged. To 5 ml of the supernatant liquid are added 5 ml of $H_2O$ and 1 ml of the reagent and readings are made against a blank. These follow the Beer-Lambert law for 0 to 22 mg of PVP per 100 ml of plasma. The variation from the correct values was $<$ 4 per cent. in 95 per cent. of the tests. CHEM. ABSTR.

3142. **Micro-estimation of porphyrins in bones, teeth and shells.** T. K. With (*Biochem. J.*, 1955, **60** [4], 703–704).—A very simple method for the micro-determination of porphyrins in bony structures is described. Not more than 50 mg of material are needed. This is powdered with a saw or file, and the powder, without previous de-fatting, is extracted with 0·5 *N* HCl. The extracts are centrifuged and the porphyrins are determined in the extract by a standard spectrophotometric procedure. J. N. ASHLEY

3143. **Bile acids and steroids. XXII. A method for the estimation of the taurine content and its conjugation with cholic acid in rat liver.** J. Bremer (*Acta Chem. Scand.*, 1955, **9** [4], 683–688).—The determination of taurine and taurine conjugates with cholic acid in rat-liver homogenates is made by the use of $^{35}S$-labelled taurine. The measurement of taurocholic acid formed is based on a selective extraction of taurocholic acid with *n*-butanol, while the free taurine remains almost quantitatively in the water phase.

O. M. WHITTON

3144. **An enzymic estimation of glutathione.** T. Wieland, K. Dose and G. Pfleiderer (*Biochem. Z.*, 1955, **326** [6], 442–445).—A method for the estimation of glutathione is described, based on the formation of S-lactoyl-reduced glutathione, which shows strong absorption in the u.v. range, with a maximum at 235 mμ. The following quantities are used: methylglyoxal (1 per cent.), 0·1 ml; reduced glutathione, 0·02 to 0·1 ml; glyoxalase I, 0·1 ml; 0·067 *N* phosphate buffer (pH 6·3), 3·2 to 3·28 ml. A suitable temperature is 20° C, and extinction is measured at 240 mμ. In a test, a soln. of reduced glutathione containing 826 μg per ml was used. The calibration curve is linear over a range 0 to 26 μg per ml. The glyoxalase is prepared according to the method of Wieland and Köppe (*Annalen*, 1953, **581**, 1).

G. W. CAMBRIDGE

3145. **The determination of glutathione in blood and tissues.** S. K. Bhattacharya, J. S. Robson and C. P. Stewart (*Biochem. J.*, 1955, **60** [4], 696–702).—The iodimetric and glyoxalase methods are applicable to the determination of reduced glutathione in blood, but only the enzymic method gives reliable results with tissues. Slight modifications in the method of Dohan and Woodward (*Brit. Abstr. A II*, 1939, 410) are suggested for the accurate determination of total glutathione (reduced + oxidised) in blood, using the glyoxalase method and electrolytic reduction. These include the use of 3 per cent. (instead of 2 to 2·3 per cent.) sulphosalicylic acid as the protein precipitant in the electrolytic reduction procedure. The iodimetric method is unreliable for the determination of total glutathione in blood, because interfering substances are liberated during the electrolytic reduction.

J. N. ASHLEY

3146. **The quantitative estimation of amino nitrogen by determination of bound copper with the flame photometer.** R. E. Beauchene, A. D. Berneking, W. G. Schrenk, H. L. Mitchell and R. E. Silker (*J. Biol. Chem.*, 1955, **214** [2], 731–739).—A simple, rapid method for the analysis of amino acids is described; it is based on the formation of a Cu complex and the determination of the Cu with a flame photometer. It is more rapid than the spectrophotometric method because reaction of the Cu complex with diethyldithiocarbamate and the subsequent extraction with *iso*amyl alcohol and centrifugation are eliminated. The amino-acid solution or protein hydrolysate is treated with an aq. suspension of copper phosphate. After removal of excess of copper phosphate, an aliquot of the supernatant liquid is subjected to flame photometry. The amount of Cu, and hence of amino acid, is ascertained from a standard graph.

J. N. ASHLEY

3147. **A simpler and better method for the quantitative estimation of amino acids and peptides by means of the ninhydrin-copper complex.** F. Bode (*Biochem. Z.*, 1955, **326** [6], 433–435).—The following method is claimed to give better localisation of amino acids and peptides containing a free α-amino group. Chromatograms are run on paper with *n*-butanol - $H_2O$ - acetic acid, and sprayed with a ninhydrin solution (ninhydrin, 0·5 g per 100 ml of acetone, 90 parts; $H_2O$, 5 parts; acetic acid, 5 parts). After being dried for 15 min. at 90° C, the paper is treated with copper solution [saturated copper nitrate soln. (1 ml), $NaNO_3$ soln. (65 per cent.) (0·02 ml) and acetone (100 ml)]. The spots are a salmon-red colour and are eluted with methanol (8 ml) and estimated at 530 mμ.

G. W. CAMBRIDGE

3148. **Chromatography combined with automatic recording of electrolytic conductivity. IV. Elution analysis of some amino acids, amines and alkali metals on Dowex 50 in various solvents.** B. Drake (*Ark. Kemi*, 1955, **8** [2], 171–188).—Results are recorded for the chromatographic separation and determination of amino acids, amines, $NH_4^+$ and alkali metals on Dowex 50 in carrier solutions of HCl or alkali chlorides. The effects of concn. of the HCl, etc., and of additives such as ethanol or formaldehyde, are described. The use of buffer solutions with conductivity recording has been attempted, but citrate buffers produce a very unsteady base-line, although phosphate buffers produce a serviceable recording. The effect of different concentrations of acid or alkali chloride

on peak shape or position is discussed. The elution vol. of the peak of many substances varies approx. inversely with the concn. of electrolyte, but the rule is by no means general. A theoretical formula for elution vol. for uni-uni-valent salts is derived, and the comparison of peak areas in different examples is discussed. E. J. H. BIRCH

3149. **Chromatography combined with automatic recording of electrolytic conductivity. V. Model experiments on gradient elution analysis.** B. Drake (*Ark. Kemi*, 1955, **8** [2], 189–196).—The difficulty of the changing base-line in the conductivity recording of elution analysis is overcome by using two mixing chambers (described) in series and adding to the increasing concentration of HCl an increasing concentration of glycerol, whose viscosity reduces the conductivity and keeps the base-line, though not straight, within the confines of the chart. Trial experiments on the elution of alkali metals are described. E. J. H. BIRCH

3150. **Paper electrophoresis as a quantitative method. Serum proteins.** W. P. Jencks, M. R. Jetton and E. L. Durrum (*Biochem. J.*, 1955, **60** [2], 205–215).—A detailed procedure for the paper-electrophoretic analysis of serum proteins is described. The amount of bromophenol blue bound by denatured proteins on filter-paper depends on the time of heat denaturation, time of staining, and amount of rinsing. These differ for different proteins. By this method a linear relationship is given between dye uptake and protein concn., which does not depend on the area of application of the protein; it allows satisfactory reproducibility in separate determinations of percentage distribution of albumins and globulins, and it provides a sufficiently intense stain to minimise errors due to background variations. J. N. ASHLEY

3151. **Simple paper-chromatographic method for the study of serum-protein patterns in health and disease.** K. V. Giri (*Experientia*, 1955, **11** [4], 165–166).—A circular paper is used (Whatman No. 1 filter-paper, 18·5 cm in diam.) and 40 $\mu$l of the serum are spotted at its centre. The wick is inserted at the centre of the paper and the chromatogram is developed with 40 per cent. aqueous ethanol as the solvent. The spot should not be allowed to dry before development. After the solvent front reaches a distance of 8 cm from the centre, the paper is dried at 90° to 100° C for about 5 min. The protein fractions are delineated as channelled and circular zones by staining with bromophenol blue. A good comparison of the difference in the patterns showing the variation in albumin to globulin ratio is produced by a mixed chromatogram, spotting 10 $\mu$l of normal and pathological serum diametrically opposite to each other on the circumference of a circle (3 cm in diam.) drawn at the centre of the paper. Visual chromatographic patterns showing the variations in the albumin - globulin fraction are in agreement with the electrophoretic patterns obtained. R. S. TONKS

3152. **Accuracy and reproducibility of paper protein electrophoresis [of blood plasma].** R. A. Neely and D. W. Neill (*Nature*, 1955, **176**, 33–34).—Protein-free plasma was obtained by heating pooled human plasma for 3 min. in a bath of boiling water and centrifuging for 2 hr. at 3000 r.p.m. Bovine serum albumin (Armour) and bovine globulin (Armour, fraction V) were dissolved in this soln. to a concn. of 6 g of protein per 100 ml in each case. These stock soln. were diluted with protein-free plasma to give concn. of 4 g and 2 g of albumin and globulin, respectively, and then mixed in various proportions. The mixtures (2·5 cu. mm) were applied to each of five spots along a line at right-angles to the axis of strips of Whatman No. 1 filter-paper. Electrophoresis was carried out by the method of Grassman *et al.* (*Dtsch. med. Wochschr.*, 1951, **76**, 333). The serum-bearing end of the paper was placed on the cathode side of the tank and migration was continued for 16 hr. at 110 V. After being dried rapidly in hot air at 125° C, strips were dyed either for 10 min. in saturated naphthalene black 12 B in methanol containing 10 per cent. of glacial acetic acid, or for 30 min. in 0·1 per cent. bromophenol blue in absolute ethanol saturated with $HgCl_2$. Further details for treating the dyed strips are given, as well as conditions governing the concn. of the protein solutions. Naphthalene black 12B gives the more correct and reproducible evaluation of protein composition. P. HAAS

3153. **Quantitative determination of thiol groups in proteins.** O. Pihar (*Chem. Listy*, 1953, **47**, 1647–1651).—A specific and accurate method for the determination of thiol groups in proteins is described; it is based on the reaction of a buffered protein soln. with 0·0001 *M* sodium chloromercuribenzoate (**I**) and on potentiometric titration of the small excess of **I** with 0·0001 to 0·0005 *M* cysteine, a silver electrode being used. The method, which allows the determination of thiol groups in a protein concn. range of $10^{-8}$ to $10^{-7}$ mole with an accuracy of $\pm$ 0·03 $\mu$g, is suitable for the analysis of native or partly denatured proteins. A procedure is given for ascertaining the excess of **I**, which can be used without denaturing the protein; this method also makes it possible to distinguish between a specific and non-specific inhibitory effect of **I** towards the individual thiol enzymes. Native human-serum albumin was found to contain no free thiol groups. G. GLASER

3154. **Determination of thiol groups in human albumin and in plasma.** O. Pihar (*Chem. Listy*, 1953, **47**, 1652–1656).—The method in which sodium chloromercuribenzoate (**I**) is added to a soln. of a protein and the excess of **I** is determined by potentiometric titration with cysteine (*Anal. Abstr.*, 1955, **2**, 3153), has been applied to the study of the thiol-group content of human-serum albumin and of plasma. It is concluded that no free thiol groups occur in native human-serum albumin but that, owing to the denaturing effect of **I** in concn. $>$ 0·00045 *M*, the formation of 0·8 mole of thiol groups per mole of albumin becomes evident. To determine thiol groups in plasma, centrifuge a mixture of blood (0·2 ml) and physiological salt soln. (1·8 ml), add the diluted plasma (1·5 ml) to a mixture of 0·0005 *M* **I** (1 ml) and 0·1 *M* $Na_2HPO_4$ (4·5 ml), and titrate the excess of **I** potentiometrically with 0·0005 *M* cysteine, a silver electrode being used. G. GLASER

3155. **Polarography of di- and tri-phosphopyridine nucleotides.** C. Carruthers and J. Tech (*Arch. Biochem. Biophys.*, 1955, **56** [2], 441–447).—A study is made of the polarography of di- and tri-phosphopyridine nucleotides (DPN and TPN, respectively) and of nicotinamide mononucleotide (NMN) in 0·5 *M* tri(hydroxymethyl)methylamine buffer, adjusted if necessary to between pH 10·3 and 10·6 with *N* NaOH. Under these conditions the three compounds have $E_{\frac{1}{2}} = -0{\cdot}98$, $-1{\cdot}23$ and $-1{\cdot}14$ V, respectively, *vs.* the S.C.E. These values are independent of, and the diffusion current for each

is proportional to, concn. The procedure gives reliable results for DPN in the presence of TPN, but only approx. results for TPN in the presence of DPN. Details are given for the prep. of $HPO_3$ extracts of liver and for the separation of interfering substances by chromatography.
W. H. C. SHAW

3156. **Nucleotide metabolism. IV. The phosphorylation of 5′-uridine nucleotides by cell fractions from rat liver. [Separation and determination of nucleotides.]** E. Herbert, V. R. Potter and Y. Takagi (*J. Biol. Chem.*, 1955, **213** [2], 923–940).—An anion-exchange method is described for the separation of the uridine and adenosine nucleotides in various cell fractions. It is based on chromatography on manually operated Dowex 1 (X10) formate anion-exchange columns. The resolving power of the two formate systems usually employed (see Hurlbert *et al.*, *Ibid.*, 1954, **209**, 23) is combined in a single chromatogram. After elution, the nucleotides are determined spectrophotometrically at 260 m$\mu$.
J. N. ASHLEY

3157. **A reagent for the detection of chloride and of certain purines and pyrimidines on paper chromatograms.** T. Wood (*Nature*, 1955, **176**, 175–176).—The reagent is prepared by dissolving 0·2 g of bromophenol blue in 50 ml of acetone and adding an equal volume of 2 per cent. $AgNO_3$ soln.; it is stable for one week. Chromatograms were run in butanol - acetic acid - water (60:15:25), dried, treated with ammonia vapour (to prevent a "fast" staining of the lower regions of the paper) and the excess of ammonia was removed in a current of air. After dipping the papers in the reagent and drying them at room temperature, they were rinsed in water until the background was white or pale blue. The spots were marked while the paper was still damp. Chloride (as little as 1 $\mu$g), bromide and iodide showed as rose spots ($R_F$ = 0·20), which became violet as the paper dried. Purines, pyrimidines and other substances capable of giving a spot showed up blue. It is suggested that the distinctive colour obtained with these halogen ions, in conjunction with their $R_F$ values, will serve to demonstrate their presence on a chromatogram. Detectable amounts are adenine, guanine, xanthine and hypoxanthine, 0·5 $\mu$g; adenylic acid, 1 $\mu$g; potassium chloride, 2 $\mu$g; cytosine, 5 $\mu$g. Uric acid, uracil, thymine, cytidylic acid and sodium barbitone did not react. For chloride only, the coloured spot was more obvious if 5 ml of the reagent were diluted with 95 ml of 1 per cent. $AgNO_3$ in aqueous acetone. The use of the reagent for detecting compounds that form an insoluble complex with silver, *e.g.*, thiophenyl $\beta$-benzyloxycarbonylaminopropionate, is suggested.
O. M. WHITTON

3158. **Fractionation of phosphates by paper ionophoresis and chromatography.** H. E. Wade and D. M. Morgan (*Biochem. J.*, 1955, **60** [2], 264–270).—Methods are described for the fractionation of mixtures of acid-sol. phosphates by paper ionophoresis and paper chromatography, and by a combination of these processes, using a solvent system composed of aq. *n*-butyric acid and Na butyrate at pH 3·5. The method provides for the location and recovery of the fractions separated, and facilitates their identification because the use of nitrogenous reagents is avoided. Data are given for the behaviour of 53 acid-sol. phosphates of biological interest. Creatine phosphate and acetyl phosphate slowly decompose during movement on filter-paper under the specified conditions, and dihydrodiphosphopyridine nucleotide is slowly oxidised to diphosphopyridine nucleotide.
J. N. ASHLEY

3159. **Quantitative chromatographic determination of labelled phosphorus derivatives and their turnover rate in biological systems.** O. Lindberg and L. Ernster (*Sci. Tools*, 1955, **2** [1], 7–11).—A procedure is described for the quant. determination of concn. and turnover rate of small amt. of phosphorylated intermediates in biological systems. It involves (*a*) incubating the system in the presence of a known concn. of radioactive P; (*b*) chromatographic separation of the phosphorus derivatives formed; (*c*) radio-assay of the chromatogram; and (*d*) computation of the concn. of the derivatives. For the estimation of the turnover rate it is also necessary to incubate the same system as in (*a*) in the presence of the same phosphate source, without radioactivity. When a steady state is reached, a minute amount of the labelled precursor is added and, after chromatographic separation, the rate of appearance of radioactivity in the metabolite under consideration is measured. The turnover rate from the results obtained is computed. The sensitivity, uses and limitations of the method are discussed.
A. M. SPRATT

3160. **Determination of small amounts of total cholesterol by the Tschugaeff reaction, with a note on the determination of lathosterol.** H. K. Hanel and H. Dam (*Acta Chem. Scand.*, 1955, **9** [4], 677–682).—A simple sensitive method for the determination of cholesterol, based on Tschugaeff's colour reaction with acetyl chloride and zinc chloride (*Ber.*, 1909, **42**, 4631), is described. The sample, *e.g.*, 200 to 300 $\mu$l of bladder bile (or 2 to 3 ml of fistula bile) or 0·5 g of liver, is saponified with KOH (17 per cent.) in 50 per cent. ethanol and extracted with light petroleum. After drying over anhyd. $Na_2SO_4$ and evaporating the solvent, the residue is transferred with $CHCl_3$ to a test-tube and the solvent is evaporated to a vol. of $\simeq$ 2 ml. After the addition of 1 ml of the $ZnCl_2$ reagent and 1 ml of acetyl chloride, the tube is heated at 65°C for 15 min. The cooled liquid is made up to 5 ml and the colour measured within 30 min. at 528 m$\mu$. Standards are prepared with each test. Cholestanol and *epi*cholestanol give no colour. Coprostanol gives a faint reaction with absorption maximum at the same wavelength as cholesterol, but with absorbance about one-tenth of that of cholesterol. Cholic, deoxycholic, chenodeoxycholic, glycocholic and taurocholic acids give a yellowish-brown colour reaction, their maximal absorbance being in the interval 375 to 450 m$\mu$. As little as 0·004 mg of cholesterol per ml of reaction mixture can be determined with an accuracy of about 3 per cent. 7:8-Cholesten-3-ol (lathosterol) gives a yellow colour reaction under the same conditions as cholesterol with absorbance maximum of 395 m$\mu$, and almost no absorbance at 528 m$\mu$ where cholesterol yields maximum absorbance. Cholesterol and lathosterol may be determined simultaneously by the present method.
O. M. WHITTON

3161. **A chemical method for the determination of oestriol, oestrone and oestradiol in human urine.** J. B. Brown (*Biochem. J.*, 1955, **60** [2], 185–193).—A new chemical method is described for the separate determination of oestriol, oestrone and oestradiol-17$\beta$ in the urine of men and non-pregnant women. It involves hydrolysis with boiling conc. HCl, extraction with ether, and a new phase-change

purification of the phenolic fraction. This depends on methylation of the phenolic group with dimethyl sulphate in borate buffer at pH 10 to 11·5 and 37° C. The oestrogen methyl ethers are separated by chromatography on $Al_2O_3$, and are determined colorimetrically by using an improved Kober colour method and spectrophotometric correction for interfering chromogenic material. The method is reproducible, and the results are significant even when the urine contains only small amounts of oestrogens. One person, unaided, can carry out 4 to 6 determinations in two days. J. N. ASHLEY

3162. **Blood steroids.** J. Schwartz and E. Pivel (*Ann. Endocrinol.*, 1954, **15** [4], 554–558).—A modified Gardner method (*J. Clin. Endocrinol.*, 1953, **13**, 941) is recommended. *Procedure*—Heparinised plasma (10 ml) is acidified with 25 ml of 10 per cent. HCl and the mixture is hydrolysed under reflux for 12 min. The cooled hydrolysate is extracted three times with 25 ml of ether and the combined extracts are washed twice with 20 ml of 10 per cent. NaOH soln. and twice with 20 ml of water. The washed extract is evaporated to dryness and the residue is dissolved in 20 ml of 70 per cent. ethanol. The resulting solution is washed three times with 15 ml of light petroleum, the washings being discarded. To the washed ethanolic extract are added 10 ml of water and the product is extracted three times with 15 ml of chloroform. The combined chloroform extracts are evaporated to 12 ml on a bath of boiling water, then put on a column of Florisil (3 g of chloroform-suspended Florisil in a tube 1 cm in diameter). Elution is effected with 35 ml of chloroform and the eluate is evaporated to dryness in the flask in which the Zimmermann reaction is carried out. The absorption of the coloured end-product is read in a photo-electric absorptiometer at wavelengths of 460, 520 and 580 m$\mu$, and the corrected extinction value is calculated from Allen's formula. Recoveries are said to be 80 to 103 per cent., and the daily variation for normal men was found to be from 46 to 80 $\mu$g per 100 ml of plasma. E. KAWERAU

3163. **Determination of 17-hydroxycorticosteroids in human peripheral blood.** A. A. H. Kassenaar, A. Moolenaar and J. Nijland (*Acta Endocrinol.*, 1955, **18**, 60–66).—Extract 20 ml of plasma with chloroform (3 × 30 ml), evaporate the chloroform *in vacuo*, add 3 ml of methanol (70 per cent.) and extract with toluene - hexane (1 : 1) (3 × 2 ml). Extract the methanol phase with pentane (2 × 2 ml), dry the methanol phase *in vacuo*, add 10 ml of ethyl acetate and extract once with $Na_2CO_3$ soln. (5 per cent.). Extract the ethyl acetate soln. with 0·5 *N* HCl saturated with NaCl, evaporate the ethyl acetate in a stream of N and dissolve the residue in 0·3 ml of methanol for colorimetry. Add 2·6 ml of $H_2SO_4$ (60 per cent.), heat for 5 min. at 60° C, cool, and measure the extinction in a Beckman spectrophotometer between 370 and 460 m$\mu$ at 10-m$\mu$ intervals. Then heat the contents of the cuvettes with 0·1 ml of $H_2SO_4$ containing 1·75 mg of phenylhydrazine hydrochloride for 20 min. at 60° C, and take readings at the same wavelengths as before. A standard of cortisone (5 $\mu$g in 0·3 ml of methanol with 2·6 ml of 60 per cent. $H_2SO_4$ and 0·1 ml of phenylhydrazine reagent) is included. From the difference in the readings after the first and second heatings a corrected absorption curve is obtained for the compounds in the plasma that react with phenylhydrazine. The 17-hydroxycorticosteroid content is calculated, by the Allen method, from the resulting curve and that obtained with the standard. Normal human plasma contains 6·8 ± 1·4 $\mu$g per 100 ml in males, and 6·2 ± 1·5 $\mu$g in females. CHEM. ABSTR.

3164. **Elimination of colouring disturbing factors in the determination of 17-ketosteroids after chromatographic separation.** W. Spiegelhoff, D. Weber, K. H. Wiedehage and O. Ortiz (*Acta Endocrinol.*, 1955, **18**, 47–59).—The elimination of disturbing colour factors from the urine as found in the chromatographic method of Dingemanse (*J. Clin. Endocrinol.*, 1946, **6**, 535) by calculation gives large differences between total values and the sum of the various fractions. The following method is proposed. The dry residue of the urine extract is dissolved in benzene (50 ml) and chromatographed as described. A 10-ml portion of each 50-ml eluate is evaporated to dryness, the residue is dissolved in ethanol (0·2 ml), and 2 per cent. *m*-dinitrobenzene in ethanol (0·2 ml) and 3 *N* KOH (0·2 ml) are added. The colour develops during 1 hr. in the dark at 25° C. The coloured mixture is added to chloroform - ethanol (3 : 1) (6 ml) and filtered through a soft filter containing a small quantity of $Na_2SO_4$ in the tip. A clear filtrate is thus obtained which is measured at 500 m$\mu$. The hormone content is calculated from a standard curve prepared with dehydro*iso*androsterone.
CHEM. ABSTR.

3165. **Micro-determination of corticosteroids with tetrazolium derivatives.** W. Nowaczynski, M. Goldner and J. Genest (*J. Lab. Clin. Med.*, 1955, **45** [5], 818–821).—The use of 2 : 3 : 5-triphenyltetrazolium chloride (**I**) and of 3 : 3′-(3 : 3′-dimethoxy-4 : 4′-diphenylene)di-(2 : 5-diphenyltetrazolium chloride) (blue tetrazolium) (**II**) for the micro-determination of corticosteroids and for their detection on paper chromatograms is investigated. The **II** reagent is preferred in the two quantitative procedures described. One procedure requires 5 to 30 $\mu$g of corticosteroids and the colours are developed with buffered **II** reagent at 90° C. The other, carried out at room temp., requires 10 to 50 $\mu$g. The intensity of colour is dependent on temp. and pH. Small differences in the wavelength of maximum optical density are caused by variations in the purity of **II**. By the procedures recommended, the sensitivity and the stability of the final colour are increased. Spray reagents for detecting 0·25 $\mu$g of corticosteroids per sq. cm (with **II**) or 2 to 5 $\mu$g per sq. cm (with **I**) on paper chromatograms are described. W. H. C. SHAW

3166. **Determination of reducing corticosteroids in adrenal extracts.** Z. Pádr, M. Šmíd and O. Sibliková-Zbudovská (*Československ. Farmac.*, 1955, **4** [2], 60–62).—The drawbacks of current colorimetric methods are discussed. Reducing impurities present in most raw extracts invalidate the results, as the reagents used, 2 : 3 : 5-triphenyltetrazolium chloride (**I**) and 3 : 3′-(3 : 3′-dimethoxy-4 : 4′-diphenylene)di-(2 : 5-diphenyltetrazolium chloride) (blue tetrazolium) (**II**) are non-specific. Paper chromatography, followed by treatment with **I**, cutting out and eluting of the various coloured portions, and subsequent determination was found subject to many errors and gave too high results. The chromatogram was therefore eluted without carrying out the colour reaction *in situ*. Two identical samples were chromatographed side by side. One was used for detection with **I** and **II** and the other was cut out accordingly. The cuttings were separately eluted and determined

colorimetrically. The method was found quant. to ± 5 per cent. or better for many corticosteroids, though colour calibration curves are given for only two of these; they are in good agreement with published results. The chromatography was carried out on Whatman No. 1 paper impregnated with formamide, the developing solution was benzene - chloroform (4 + 1), and the eluting agent was 96 per cent. ethanol. A. O. JAKUBOVIC

3167. **Corticosteroids in the urine of normal and scorbutic guinea-pigs: isolation and quantitative determination.** S. Burstein, R. I. Dorfman and E. M. Nadel (*J. Biol. Chem.*, 1955, **213** [2], 597–608).—Normal and scorbutic guinea-pig urines contain cortisol, 6β:11β:17α:21-tetrahydroxypregn-4-ene-3:20-dione (6β-hydroxycortisol), and an as yet unidentified steroid. After separation by paper partition chromatography with a chloroform - formamide system the three steroids are determined spectrophotometrically at 240 ($E^{1\%}_{1cm}$ 413), 237 ($E^{1\%}_{1cm}$ 270) and 240 mμ ($E^{1\%}_{1cm}$ 384), respectively. J. N. ASHLEY

3168. **A simplified method for the determination of formaldehydogenic substances in biological material.** E. Demey-Ponsart, J. Faidherbe, R. Vivario, C. Heusghem and H. van Cauwenberge (*Ann. Endocrinol.*, 1954, **15** [4], 614–621).—The side-chain of $C_{21}$ steroids is oxidised with $HIO_4$ and the liberated formaldehyde is determined with chromotropic acid, as described by MacFayden (*J. Biol. Chem.*, 1945, **158**, 107). Distillation is avoided by carrying out this stage in a Conway unit. Blood steroids are extracted from 5 to 20 ml of plasma with an ethanol - ether mixture (3:1). This extract is enriched with ethanol, then washed with light petroleum and further purified by precipitation of the phospholipids with acetone saturated with $MgCl_2$. The extract is evaporated to dryness and redissolved in 0·5 ml of glacial acetic acid, of which 0·2 ml is used in the outer compartment of the Conway unit. The centre compartment of the unit is charged with 3 ml of chromotropic acid reagent (0·2 per cent. of chromotropic acid in 12·5 *M* $H_2SO_4$), and the outer compartment receives, without mixing, on one side 0·5 ml of $SnCl_2.2H_2O$ solution and on the other 0·5 ml of $HIO_4$ (0·01 *M* $KIO_4$ in 0·15 *M* $H_2SO_4$). The steroid extract (0·2 ml) is carefully added to the periodate in the unit and set aside for 30 min. at room temperature; the process is then arrested by a rotary motion, which allows the $SnCl_2.2H_2O$ solution to mix with the contents in the outer compartment. The units are now left in the incubator at 35° C overnight. An aliquot is then removed from the centre compartment, immersed for 30 min. in a bath of boiling water, cooled and the resulting colour is read at 570 mμ. Formaldehyde standards are prepared from the acid hydrolysate of purified hexamine, and a blank test, omitting the periodate, is run. Recovery of formaldehyde was quantitative. Normal blood and urine values for formaldehydogenic steroids of men and women are quoted. E. KAWERAU

3169. **Determination of the activity of the cholinesterases in human blood.** A. Meyer and W. Wilbrandt (*Helv. Physiol. Acta*, 1954, **12**, 206–216).—A modification of the electrometric method of Michel (*J. Lab. Clin. Med.*, 1949, **34**, 1564) for plasma and red-cell cholinesterases which requires a much smaller quantity of blood, is described. In a further simplification of this method butyrylcholine is used as specific substrate, thus permitting the determination of plasma cholinesterase in unseparated blood. Another method is presented in which the enzymic release, under specified conditions, of thiocholine (**I**) from acetylthiocholine (**II**) or butyrylthiocholine (**III**) is measured by simple iodimetric titration. (The SH of the freed **I** is oxidised to S·S by iodine.) The activity of plasma cholinesterase is determined in unseparated blood with the specific substrate **III**, and the activity of red-cell cholinesterase is determined after inhibition of plasma cholinesterase with Diparcol (diethazine hydrochloride), with **II** as substrate. CHEM. ABSTR.

3170. **Activity of cholinesterases. I. Spectrophotometric estimation of the activity.** Jean Grégoire, Jana Grégoire and N. Limozin (*Bull. Soc. Chim. Biol.*, 1955, **37** [1], 65–79).—A solution containing a weak buffer, phenol red and the enzyme or serum is added to a solution of acetylcholine hydrochloride in a cuvette at 25° C; the optical density at 558 mμ is measured every 30 sec. for ≃ 10 min. From the initial rate of change the activity of the cholinesterase is evaluated by reference to a calibration curve, obtained by measuring the optical density of the buffered phenol red in the presence of known amounts of acetic acid. A correction is applied for the spontaneous hydrolysis of acetylcholine. It is shown that phenol red has no effect on the rate of hydrolysis, and the method gives results in satisfactory agreement with the manometric method of Ammon (*Arch. Ges. Physiol.*, 1933, **233**, 486). The precision is ≃ ± 5 per cent. at low concn. of substrate ($2 \times 10^{-4}$ *M*), and better at higher concn.; it is not suitable for highly coloured solutions, but is more convenient than the manometric method, particularly for the determination of initial velocities at low substrate concn. H. P. PAGET

3171. **New enzymological methods. I. Photometric determination of the cytochrome oxidase activity.** O. Pihar (*Chem. Listy*, 1953, **47**, 1511–1515).—Two rapid photometric methods for the determination of the activity of cytochrome oxidase saturated with cytochrome-*c* are described; they are based on the oxidation of leucodichlorophenolindophenol (**I**) and of *p*-phenylenediamine (**II**) to coloured products. The latter method is more broadly applicable, giving reliable results even with homogenates from the kidney and heart of the rat, whilst the former method cannot be applied to samples containing reducing components. *Procedure*—To the enzyme preparation (0·1 ml) add 0·0001 *M* cytochrome-*c* (0·3 ml) and 0·1 *M* phosphate buffer (pH 7·3) (2·1 ml), followed by a soln. of **I** (0·5 ml), prepared by reducing 0·0005 *M* dichlorophenolindophenol with sodium amalgam. Measure the extinction at 610 mμ in 30-sec. intervals during 3 min. The apparent activity of a control experiment, in which the soln. contains, in addition to the same system, 0·01 ml of 0·033 *M* NaCN (added before **I**), must be subtracted. Similarly, measure the extinction at 640 mμ of a system containing 0·1 *M* phosphate buffer (pH 7·3) (1 ml), 0·2 per cent. fresh aq. **II** (2 ml), the enzyme preparation (0·1 ml) and 0·0002 *M* cytochrome-*c* (0·3 ml). G. GLASER

3172. **New enzymological methods. II. Photometric determination of xanthine oxidase activity.** O. Pihar and K. Fischer (*Chem. Listy*, 1953, **47**, 1862–1864).—The activity of xanthine oxidase was conveniently determined by measuring, at 610 mμ

and at intervals of 30 sec., the extinction of solutions of the enzyme (obtained from milk) with dichlorophenolindophenol (**I**). The determinations were carried out on a system consisting of the enzyme soln. (1 ml), a 0·0005 *N* soln. of **I** (0·3 ml), 0·05 *M* $Na_2HPO_4$ (0·85 ml) (pH 7·3), 0·1 *M* $KH_2PO_4$ (0·45 ml), 0·03 *M* NaCN (0·1 ml) and 0·005 *M* xanthine in 0·1 *N* NaOH (0·3 ml). The pH of the system is 6·9.

G. GLASER

3173. **The quantitative histochemistry of brain. IV. Lactic, malic and glutamic dehydrogenases. [Determination of these enzymes.]** J. L. Stromінger and O. H. Lowry (*J. Biol. Chem.*, 1955, **213** [2], 635–646).—Micro-methods are described for the determination of lactic, malic and glutamic dehydrogenases in 0·2 to 3 μg of dried brain. The assays are based on the measurement of the rate of reduction of diphosphopyridine nucleotide in the presence of the appropriate substrate; the determination is effected spectrophotometrically at 340 mμ.

J. N. ASHLEY

3174. **Determination of total carbon and its radioactivity. II. Reduction of required voltage and other modifications.** F. M. Sinex, J. Plazin, D. Clareus, W. Bernstein, D. D. Van Slyke and R. Chase (*J. Biol. Chem.*, 1955, **213** [2], 673–680).—The 3800 volts previously used in the gas-phase proportional counter for the determination of the specific activity of $^{14}CO_2$, as described by Bernstein and Ballentine (*Brit. Abstr. C*, 1950, 301) and by Van Slyke *et al.* (*Brit. Abstr. C*, 1952, 82), can be reduced to between 2000 and 2100 V if a mixture containing 90 per cent. of argon and 10 per cent. of methane is used instead of methane. In the method for the determination of $^{14}C$ activity by wet combustion and gas counting of the resulting $^{14}CO_2$ and $^{12}CO_2$, use of the lower voltage is advantageous, especially in humid weather in a room without humidity control. The only disadvantage is that the max. size of the carbon sample is $\simeq$ 6 mg, compared with 16 mg by the methane method. A circuit diagram is given for a non-overloading amplifier which can be used for methane or methane-argon $^{14}CO_2$ counters, or for routine scintillation or Geiger counting.

J. N. ASHLEY

See also Abstracts 3060, 3081, 3239, 3240, 3244, 3246.

## Drugs

3175. **Paper chromatography in qualitative pharmaceutical analysis.** J. Büchi and M. Soliva (*Pharm. Acta Helv.*, 1955, **30** [4], 154–174).—A scheme is given for the systematic paper-chromatographic analysis of pharmaceutical or forensic samples. Classical methods are briefly discussed and compared with chromatographic methods. The theory of paper chromatography, effect of dissociation or association, concentration, temperature and formation of complexes are examined, and the techniques and materials used are described.

P. S. STROSS

3176. **Pressed-bromide method of infra-red spectrographic analysis of narcotics.** J. J. Manning (*Bull. Narcotics, U.N., Dep. Social Affairs*, 1955, **7** [1], 85–100).—An atlas of i.r. spectra of 26 natural and synthetic narcotics tested by the pressed-bromide method is given.

N. E.

3177. **Physical methods for the identification of narcotics. IVA. The infra-red spectroscopic method.** C. E. Hubley and L. Levi (*Bull. Narcotics, U.N., Dep. Social Affairs*, 1955, **7** [1], 20–41).—A summary of the history and general principles of i.r. spectroscopy is given, apparatus is described and sample-handling techniques, presentation and interpretation of data are discussed. Tables of spectra-structure correlations and characteristic bands are given. **IVB. Infra-red spectra of narcotics and related alkaloids.** L. Levi, C. E. Hubley and R. A. Hinge (*Ibid.*, 1955, **7** [1], 42–84).—An atlas of i.r. spectra of narcotic and allied drugs is given, comprising 85 spectra in mineral-oil mulls and 39 in chloroform solution.

N. E.

3178. **The determination of morphine in opium.** R. Fischer and K. Folberth (*Arzneimittel-Forsch.*, 1955, **5** [2], 66–67).—In the simple method described the opium is extracted with water on an acid alumina column, and the morphine is determined gravimetrically in the eluate as the dinitrophenyl ether in the usual way. Recovery experiments show that the yields are quantitative. Tincture of opium may be assayed similarly after removal of the alcohol.

A. R. ROGERS

3179. **A physical method for the determination of hyoscine hydrobromide in a tablet mixture.** R. Bruce Scott, E. J. Schoeb and J. M. Vandenbelt (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [6], 377–379).—A physical method is described for the determination of hyoscine hydrobromide in diphenhydramine (Benadryl) - hyoscine tablets. Twenty crushed tablets are shaken with 10 ml of absolute ethanol for 5 min. and centrifuged. The supernatant soln. (8 ml) is evaporated on a steam-bath until crystallisation occurs, then the residue is dried overnight in a vacuum-oven at 75° C. The dried residue is warmed at 50° C for 15 to 30 min. with 1 ml of NaCl-saturated dimethylacetamide and centrifuged. The resulting soln. is examined spectroscopically in the region of 11 to 12 μ, using a solvent blank. An accuracy $>$ 90 per cent. is attained, and the method is unaffected by a high proportion of diphenhydramine hydrochloride.

G. R. WHALLEY

3180. **The determination of ergot alkaloids with toluene-*p*-sulphonic acid in chloroform.** I. Gyenes (*Magyar Kém. Foly.*, 1955, **61** [3], 89–90).—This non-specific method is suitable for the determination of pure ergot derivatives. The pure compound (20 to 40 mg) is dissolved in dry pure ethanol-free $CHCl_3$, which is stabilised with 1 per cent. of light petroleum, and diluted to 50 ml. To a 5- or 20-ml portion, 1 to 3 drops of 0·1 per cent. dimethylaminoazobenzene in $CHCl_3$ are added and the soln. is titrated to a pale carnation-red colour with 0·001 to 0·005 *N* toluene-*p*-sulphonic acid in $CHCl_3$.

A. G. PETO

3181. **Paper chromatography of lanatoside C.** M. L. Frith and S. E. Wright (*Chem. & Ind.*, 1955, [10], 251–252).—When chromatograms of a lanatoside-C standard are treated with a freshly prepared solution of trichloroacetic acid in chloroform, two constituents appear, one fluorescing bluish-yellow in ultra-violet light, the other, a slower-running and more polar component, bright blue. If trichloroacetic acid containing $H_2O_2$ is used, the faster-running area fluoresces brighter blue in ultra-violet light, whereas fluorescence of the slower-travelling component is weakened considerably. When the lanatoside-C standard is chromatographed on formamide-impregnated paper strips, two areas can be detected with the trichloroacetic acid reagent. If alkaline *m*-dinitrobenzene is used to locate the glycosides, only one area is revealed, corresponding

to the faster-running, weaker-fluorescing area shown by freshly prepared trichloroacetic acid reagent. The embryonic chick-heart method of biological assay shows that the whole of the cardiac activity is associated with the faster-running, less-polar constituent. The slower-running constituent is deacetyl-lanatoside C. O. M. WHITTON

3182. **Rapid determination of rutin in drugs.** G. Dušinský (*Ceskosl. Farmac.*, 1955, **4** [2], 68–69).—Use was made of the intense yellow colour of rutin in alkaline solution for its determination by a visible-light absorptiometric method at 410 mμ, where maximum absorption occurs. Quantities up to 200 mg of rutin can be determined with an accuracy of ± 1·5 per cent. Substances such as starch, fats, saccharin, theophylline and phenobarbitone did not interfere. A calibration graph of extinction values against concentration of rutin is given. A. O. JAKUBOVIC

3183. **The determination of [constituents of] volatile oils by the critical solution temperature method.** R. Fischer and H. Resch (*Arzneimittel-Forsch.*, 1955, **5** [3], 137–141).—By mixing in a capillary tube small quantities of the sample under test with suitable reference liquids, *e.g.*, propane-1:2-diol, ethanediol or liquid paraffin, and determining the temperature at which the meniscus disappears (in a Kofler micro melting-point apparatus), the amount of the main ingredients present in the sample can be calculated by the use of a previously constructed calibration graph. Only very small quantities of sample are needed (5 to 10 mg) and the determination takes only about 15 min. The method has been applied to the determination of both free and esterified menthol in peppermint oil (error ± 0·33 per cent.), free and total eugenol in clove oil (error ± 0·45 per cent.), ascaridole in chenopodium oil (error ± 0·35 per cent.), and thymol and carvacrol in thyme oil. Calibration curves and full experimental details for these determinations are given. The menthol content of oil obtained from individual leaves of various parts of a plant of *Mentha piperita* was determined. A micro-distillation and separation apparatus is described. P. S. STROSS

3184. **Polarographic determination of penicillin in preparations.** E. Krejčí (*Ceskosl. Farmac.*, 1955, **4** [2], 73–74).—Penicillin itself is not polarographically active, but in buffers of pH < 4·5 a substance is formed that is reduced at the mercury electrode, decomposing to non-active products. Thus the polarographic waves are dependent on time elapsed from dissolving the penicillin. The amount of the active material depends on the temperature and the pH of the solution, but under constant conditions is proportional to the amount of penicillin dissolved, the height of the wave being a measure of the penicillin concentration. The current at the wave maximum is compared with that for a standard preparation under similar conditions. A number of experimental precautions are given. The results are not in good agreement and deviations of ± 10 per cent. from those obtained by microbiological methods are recorded. A. O. JAKUBOVIC

3185. **A simple colorimetric method for the determination of chloramphenicol in aqueous solution.** W. Döll (*Arzneimittel-Forsch.*, 1955, **5** [2], 97–98).—Aqueous soln. containing 2 to 50 μg of chloramphenicol per ml can be determined with an error ≯ 2·9 μg per ml by heating 1 ml to boiling point with 40 per cent. aq. NaOH (4 ml), cooling and measuring the intensity of the yellow colour produced, using a filter S42 E51. The colour is attributed to sodium *p*-nitrophenoxide; it is stable for at least four days. A. R. ROGERS

3186. **Physico-chemical methods of determining antibiotics. II. Anthrone method of determining mannosidostreptomycin.** E. M. Savitskaya, B. P. Bruns, A. A. Korobitskaya and V. D. Kartseva (*Zh. Anal. Khim., SSSR*, 1955, **10** [2], 124–127).—In carrying out the method of Kowald and McCormack (*Brit. Abstr. C*, 1950, 183) for determining D-mannose, errors up to ± 13 per cent. were observed. The following method is claimed to be accurate to ± 3 per cent. To 7 ml of the aq. solution of mannose or the streptomycin preparation are added, in a thin stream with continuous stirring, 23 ml of anthrone reagent, prepared by dissolving 0·1 g of anthrone in 100 ml of conc. $H_2SO_4$, adding 15 ml of water, and setting aside for 1 hr. before use. The solution is rapidly heated for 6 min. on a bath of vigorously boiling water, and then cooled in water containing ice. The optical density is determined at room temp., a red filter being used. The green colour of the solution is stable for 4 to 5 hr. G. S. SMITH

3187. **Determination of saccharin sodium with perchloric acid in acetic acid.** I. Gyenes and A. Váli (*Magyar Kém. Foly.*, 1955, **61** [3], 90–91).—In acetic acid, saccharin sodium (**I**) decomposes into *o*-sulphamylbenzoic acid and Na acetate; the acetate ions are titrated with $HClO_4$. *Procedure*—Dissolve 200 mg of **I** in anhydrous acetic acid; for each 10 ml of the soln., add 1 drop of a 1 per cent. crystal violet soln. in acetic acid and titrate with 0·1 *N* $HClO_4$ (in acetic acid) to blue (first colour-change) or an emerald-green colour (second colour-change). The $HClO_4$ is standardised against diphenylguanidine, to the same colour-change. 1 ml of 0·1 *N* $HClO_4$ ≡ 20·52 mg of **I**. The error is ± 0·5 per cent. A. G. PETO

3188. **Paper chromatography of mixtures of saccharin with dulcin.** A. Castiglioni (*Z. anal. Chem.*, 1955, **145** [3], 188–189).—By using a mixture (4:1) of butanol with aq. $NH_3$, sp. gr. 0·88, on Whatman No. 1 paper at 15° to 18° C, saccharin has an $R_F$ value of 0·3 whilst the $R_F$ value for dulcin is 0·8. For dulcin, the chromatogram is developed with $HNO_3$, an intense yellow colour being produced. Saccharin is developed with Gandini's reagent (*Brit. Abstr. C*, 1946, 194), consisting of an ethanolic soln. of 1-naphthylamine acidified with acetic acid containing a trace of copper; a bluish-violet coloration is given. P. HAAS

3189. **Identification of barbiturates by ultra-violet absorption.** J. R. Mahler and R. F. Puckett (*J. Lab. Clin. Med.*, 1955, **45** [5], 806–817).—The u.v. optical-density-difference method of Goldbaum (*Anal. Chem.*, 1952, **24**, 1604) has been investigated and extended to cover 19 commercially available barbiturates. Details are given for the extraction of the barbiturates as the sodium salts from body fluids, and for measuring and calculating the optical-density-difference ratios at selected wavelengths between 228 and 320 mμ; the ratios found are then compared with the standard values given. The use of the method in routine toxicological analysis is discussed. W. H. C. SHAW

3190. **Identification of therapeutically active barbiturates. I.** J. Büchi and X. Perlia (*Pharm. Acta Helv.*, 1954, **29** [6], 183–199).—An extraction

procedure for the isolation of barbiturates from pharmaceutical mixtures is outlined; their isolation through micro-sublimation *in vacuo* is described. **II.** (*Ibid.*, 1954, **29** [9], 265–276).—The behaviour of barbiturates during micro-sublimation *in vacuo* under various conditions is studied. Details are given, for each of the barbiturates mentioned below, of the effect of variations in the temp. of sublimation and the gradient of temp. between the hot and cold surface on crystalline form and melting point. The sublimates are examined under a microscope (32 photomicrographs), their melting points are determined, and lead, bismuth and copper complexes are prepared. Many of the complexes are characteristic and can be identified under the microscope. The following derivatives of barbituric acid are discussed in detail—5:5-diethyl, 5-*n*-butyl-5-ethyl, 5-ethyl-5-(1-methylbutyl), 5-allyl-5-*iso*butyl, 5-(β-bromoallyl)-5-*iso*propyl, 5-(β-bromoallyl)-5-*sec.*-butyl, 5-ethyl-5-phenyl, 5-ethyl-5-*cyclo*hexenyl, 5-ethyl-5-*cyclo*heptenyl, 5-ethyl-N-methyl-5-*iso*propyl, 5-*cyclo*hexenyl-5-N-dimethyl, 5-ethyl-N-methyl-5-phenyl, 5-(β-bromoallyl)-N-methyl-5-*iso*propyl, 5-ethyl-5-(1-methylbutyl)-2-thio, 5-allyl-5-*cyclo*hexenyl-2-thio. **III.** (*Ibid.*, 1954, **29** [9], 290–310).—The colour reaction of cobalt and copper salts with barbituric acid derivatives in the presence of an organic alkali and a methanol - chloroform solvent mixture is studied, and schemes are proposed for the identification of individual barbiturates. The sample is examined by using the following reagents: alkaline permanganate, formaldehyde - sulphuric acid, *m*-nitrobenzaldehyde - sulphuric acid, vanillin - sulphuric acid, *p*-dimethylaminobenzaldehyde - sulphuric acid, benzaldehyde - sulphuric acid, piperonaldehyde - sulphuric acid, furfuraldehyde - sulphuric acid, phenol - sulphuric acid and sulphuric acid. Barbiturates containing an aromatic nucleus can be nitrated, the nitro group reduced, diazotised and coupled with 2-naphthol or treated with ammoniacal hydroxylamine or alkaline acetone. The preparation of *p*-nitrobenzoyl and xanthhydrol derivatives is described and tables are given of the melting points of 18 barbiturates and their derivatives. P. S. STROSS

3191. **Complexiметric titration in pharmaceutical analysis. X. Indirect determination of amidopyrine.** B. Buděšínský (*Českosl. Farmac.*, 1955, **4** [2], 71–73).—The complexing of halides and thiocyanates of bivalent metals with *iso*pyrazolones was applied to amidopyrine (**I**). From an aqueous or 25 per cent. alcoholic solution of **I** at pH 5 to 6, the stoicheiometric complex $[Cd(\mathbf{I})](SCN)_2$ was quant. pptd. by cadmium thiocyanate. After filtering, excess of Cd in the supernatant liquid was determined by standard methods. Results for the determination of **I** in pure solution as well as in mixtures containing up to 4 components (with, *e.g.*, phenacetin, caffeine, phenobarbitone and salicylates) are given. Accuracy was normally better than ± 1 per cent., though two 3 per cent. errors are recorded. A. O. JAKUBOVIC

3192. **Complexiметric determination of Pyramidon (amidopyrine) in pharmaceutical products.** W. Groebel and E. Schneider (*Z. anal. Chem.*, 1955, **146** [3], 191–193).—Dissolve a sample containing amidopyrine (250 to 300 mg) in $H_2O$ (5 to 10 ml), boil, then add 20 ml of precipitant (5 g of $CdCl_2$ and 65 g of $NH_4SCN$ in 100 ml of $H_2O$). Neutralise with *N* NaOH to methyl red. Filter under pressure after 1½ to 2 hr. Wash with a 65 per cent. w/v soln. of $NH_4SCN$ saturated with the complex. Dissolve in conc. aq. $NH_3$ soln. (5 ml) and wash through. Add 2 ml of buffer soln. (13·5 g of $NH_4Cl$ and 88 ml of conc. aq. $NH_3$ soln. made up to 250 ml) and titrate with EDTA (disodium salt) (0·05 *M*), with Eriochrome black T as indicator (1 ml ≡ 11·57 mg of amidopyrine). Starch, if present, is first hydrolysed with HCl. R. STERN

3193. **Determinations of organic compounds in tablets and pills by infra-red spectrophotometry.** B. Salvesen, L. Domange and J. Guy (*Ann. Pharm. Franç.*, 1955, **13** [3], 208–215).—Examples are given of the infra-red spectrophotometry of tetraethylthiuram disulphide (at 7·41, 8·32, 9·92 and 10·31 μ, in $CS_2$), phenothiazine (at 7·67 and 7·97 μ, in $CS_2$), N-(2′-diethylaminoethyl)phenothiazine (at 7·77 and 8·00 μ, in $CS_2$) and N-(2′-dimethylaminopropyl)-phenothiazine (promethazine) (at 7·47, 8·00 and 8·41 μ, in $CS_2$). The error is ± 2 to 4 per cent. E. J. H. BIRCH

3194. **The chemical examination of elastic materials for suitability as closures for parenteral solutions.** K. Steiger and R. Dolder (*Pharm. Acta Helv.*, 1954, **29** [10], 311–337).—The materials are classified into three groups: the natural and synthetic rubbers, synthetic plastics, and silicone rubbers. After a detailed review of the literature, results are given of an examination (*cf.* Christiansen, *Medd. Norsk Farm. Selsk.*, 1951, **13**, 121, 131) of 26 rubber and synthetic materials. Solutions, prepared by autoclaving the finely divided test material, were then examined for appearance, smell, taste, reducing materials, heavy metals, ammonia and amines, aldehydes and ketones, organic sulphur compounds and pH changes. Of the 26 materials tested, only six complied with the chemical standards laid down, but these were unsuitable for other reasons. P. S. STROSS

See also Abstracts 2935, 3057, 3095, 3138, 3139, 3140, 3251.

## Food

3195. **New, accurate method for preparing samples of [sugar] cane for analysis.** G. R. Serbia and J. H. Fragoso (*Sugar, N.Y.*, 1955, **50** [5], 39).—The apparatus is illustrated and described. Two saws (8 in. in diam.) are mounted on the same shaft. Between these and separated by washers is a dado groover, ¼ in. wide. The cutting edge of the groover is ground so that the diameter of the groover is ≃ ¼ in. less than the diameter of the saws; this results in a non-frayed, even cut of the cane. A 1 h.p. motor drives the shaft at 3000 r.p.m.; a 40 to 50-lb sample of cane, comprising about 20 to 25 pieces, is used, each cane being cut transversely at 6-in. intervals, the shreds obtained weighing 1000 to 1500 g. Data are given comparing this, the Aguirre procedure, with the method used in Guiana at Pasudeco. The shreds obtained by the Aguirre method provide convenient samples for the determination of other constituents, such as reducing sugars, moisture and plant nutrients, in addition to the determination of sucrose, fibre, degrees Brix, etc., on samples of the cane. S. C. I. ABSTR.

3196. **Polarographic evaluation of refined sugars. Introduction of a new scale.** J. Buriánek (*Listy Cukr.*, 1955, **71**, 46–49).—The polarographic method is not suitable for general use if suitable standards for the reduction of the oxygen maximum are not available. In Vavruch's method (*Brit. Abstr. C*, 1950, 488) the need for a standard pure sucrose and

a standard molasses or other surface-active material (*e.g.*, methyl orange) introduces many difficulties. A numerical criterion now proposed is that electrical resistance which it is necessary to put in series with the polarographic vessel in order to reduce the oxygen maximum of the pure electrolyte soln. (0·002 *N* $K_2SO_4$) to a value equal to the height of the maximum for a *N* soln. of the tested refined sugar in the same electrolyte. This is called the "standard resistance" of the refined sugar. On the assumption that the ratio of the heights of the maxima with two different external resistances in the circuit is a function of the resistance which remains unchanged under different experimental conditions (*e.g.*, different polarographic instruments), it is proved mathematically that the standard resistance of a given sugar, as defined above, will also be independent of the experimental conditions. The initial assumption has been proved experimentally, with two types of polarograph and a number of different resistances and sugars in conjunction with the standard electrolyte. The method should also eliminate any differences in the water used as solvent; this was also proved experimentally, using pure water and water to which 2·5 or 5 ml of 0·025 per cent. gelatin soln. had been added per 100 ml. The determination of the "standard resistance" is thus carried out by comparing the oxygen maximum found for the normal sugar soln. in the standard electrolyte, using zero external resistance, with the values for the pure electrolyte together with external resistances from 10,000 to 100,000 ohms. The latter values can be read from a graph. A table and graph are given for converting the "standard resistance" to mg of "corrected molasses," these latter values having been obtained experimentally with pure sucrose and Vavruch's artificial standard molasses. The general experimental conditions (electrolyte and sugar concn., capillary diameter, drop time and temp.) should be those given by Vavruch (*loc. cit.*). SUGAR IND. ABSTR.

3197. **Modified Lane and Eynon method for the determination of reducing sugars.** N. R. Jones (*Brit. Food Manuf. Ind. Res. Ass. Tech. Circ.* **79**, May, 1955, 7 pp.) [Publication restricted].—The modified method was developed to give a simple rapid determination of amounts of invert sugar smaller than usual, of the order of 0·3 per cent. and upwards, in food products. The modifications combine back-titration with the constant-volume method (*Int. Sugar J.*, 1950, **52**, 185), and the quantity of sample required can thereby be much reduced. The standard Lane and Eynon reagents are used. A standard invert-sugar solution is prepared by inversion of 19 g of pure sucrose in 100 ml of water by 7·5 ml of conc. HCl for 8 days, making this up to 200 ml, neutralising 100 ml with dil. NaOH soln., acidifying with 1 ml of *N* HCl, adding 2 g of benzoic acid and diluting to 1 litre; this solution is used diluted to 5 times its vol., and then contains 2 mg of invert sugar per ml. The invert solution is used to standardise the Fehling's soln. and for the back-titration. For a preliminary titration, a suitable amount of a solution of the sample to be analysed (containing ≠ about 45 mg of invert sugar) is added to 10 ml of Fehling's soln. in a 250-ml flask, brought to the boil and titrated with the standard invert soln. until nearly all the blue colour of the Fehling's soln. has disappeared; 0·5 ml of methylene blue soln. is added and the titration is completed. The final titration is carried out similarly, except that all but about 1 ml of the invert solution, as predetermined, is added before boiling, together with water to give a final vol. of 60 ± 1 ml at the end of the titration. After boiling for 2 min. the methylene blue is added and the titration is completed in the third minute. The invert-sugar content is calculated as $I = FP - 2T$, where $I$ = mg of invert sugar in the sample, $F$ = factor of the Fehling soln. used, $T$ = titre, and $P$ = factor (derived from Lane and Eynon's figures) to correct for the wt. of sucrose in the sample. The values of $P$ for various sucrose contents are tabulated and may be plotted. SUGAR IND. ABSTR.

3198. **Rapid method for the determination of invert sugar in white and refined sugars.** J. Zaleski (*Gaz. Cukr.*, 1955, **57**, 25–26).—The colorimetric method described is based on that of Baerts and Binard (*Sucr. Belge*, 1932–33, **52**, 309), with the determination of the decolorisation of methylene blue in a fixed time. It is suitable for amounts of invert sugar < 0·05 per cent. *Procedure*—To 10 g of sugar dissolved in water in a 50-ml flask, 1 ml of alkaline K Na tartrate solution and 1 ml of 0·5 per cent. aq. methylene blue solution are added, and the mixture is made up to the mark. This mixture (15 ml) is transferred to a boiling-tube and a blank containing only K Na tartrate of the same dilution is put in another tube; the tubes are placed in boiling water and the time to complete equivalence in decolorisation is measured. The conditions must be fully standardised and exact details of the apparatus are given. A table is given for conversion of the decolorisation times to percentage invert-sugar content. The method is more rapid than the Herzfeld method.

SUGAR IND. ABSTR.

3199. **The determination of sodium bicarbonate in self-raising flours containing chalk B.P.** W. H. Stephenson and A. W. Hartley (*Analyst*, 1955, **80**, 461–470).—Experimental work is described establishing that the $NaHCO_3$ in self-raising flours made from flours containing chalk B.P. (Creta Praeparata) can be selectively decomposed by $Na_2H_2P_2O_7$. *Procedure*—The self-raising flour (17 g) is placed in a 250-ml wide-mouthed decomposition flask, which is connected with the Chittick apparatus ("Official Methods of Analysis," The Association of Official Agricultural Chemists, Washington, D.C., 1950, p. 196), warming of the flask by the hand being avoided. The stopcock is opened and the soln. in the gas burette is brought to the zero mark. After 2 min., the stopcock is closed. The levelling bulb is lowered and 45 ml of a $Na_2H_2P_2O_7$ soln. (2·5 per cent., w/v), at the same temp. as the apparatus, are run in, the level in the bulb being maintained below that in the burette during the reaction. The flask, held in cloth, is shaken vigorously and continuously for 2 min., and the apparatus is allowed to stand for 5 min., with the level in the levelling bulb 10 ml below the burette reading. The pressure is then equalised and the total vol. of gas is ascertained and the temp. and pressure are noted. The operations are repeated with an empty flask to obtain the reagent blank. If $V$ is the apparent vol. of gas from flour of unknown composition, $V_A$ the apparent vol. of gas from the acid reagent (the reagent blank) and $V_F$ the vol. of $CO_2$ yielded by the flour, then $V_F = V - V_A$, and the true percentage of $CO_2$ in the flour is given by $V_F \times$ (the factor from the A.O.A.C. tables) $\times K/100$, where $K$ is a constant determined by tests on mixtures of known composition. In the authors' laboratory $K$ is 1·1 under varying atmospheric conditions, but may need adjustment in other laboratories. A. O. JONES

3200. **Rapid determination of humidity in flour and gluten by drying in a high-frequency electrical field.** F. P. Pietermaat and E. Maes (*Fermentatio*, 1955, [1], 30–35).—Flour (2 g) and gluten (from 10 g of flour) samples are weighed, dried in a high-frequency electrical field ($4 \times 10^4$ kc.), cooled in a desiccator, and re-weighed. Drying takes 10 to 12 min. for gluten and 14 to 18 min. for flour. The results obtained in a large number of determinations by this method are compared with those obtained with the same materials by the conventional drying method (100° to 105° C for 4½ hr.) and very close agreement was obtained. S. C. I. Abstr.

3201. **Application of the thiobarbituric acid test to cereal and baked products.** E. F. Caldwell and B. Grogg (*Food Tech., Champaign*, 1955, **9** [4], 185–186).—A modification of the thiobarbituric acid test for oxidation products of unsaturated fatty acids is suggested, in which the red compound is separated from yellow interfering substances by adsorption on cellulose, followed by elution with aq. pyridine. The modified test would appear to provide a numerical index of oxidative rancidity in oat cereals and dry baked products, despite the presence of other chromogenic substances.
Brit. Baking Ind. Res. Ass. Abstr.

3202. **The estimation of the meat content of meat products.** S. Dannacher and M. Staub (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [2], 163–167).—The method is based on the isolation of the insoluble proteins, their nitrogen content being constant for a given type of meat. About 20 g of the product are accurately weighed into a centrifuge tube and extracted several times with ether, once with alcohol and finally washed with water until free of chlorides. The residue, consisting mainly of insoluble protein, is dried to constant weight and its nitrogen content is determined. The content of insoluble-protein nitrogen in the original product is calculated, and expressed as a percentage of that in the meat used for its preparation. Vegetable material will depress the nitrogen content of the residue, and its presence should be confirmed microscopically. If this consists of starch it will not affect the determination, but if it contains protein, the weight of residue is corrected by multiplying it by the ratio of its nitrogen content to that of the insoluble protein of the meat used. The following average values for the insoluble-protein contents of meats and their N contents are given: chicken 55, 15·5; oxtail 42, 15·5; ham 30, 15·4; and turtle 25·3, 16·7 per cent. When the composition of the original meat is known, as in analytical control work, the accuracy of the method is about ± 1 per cent. W. H. Parr

3203. **The use of 2:3:5-triphenyltetrazolium chloride as a test for antibiotic substances in milk.** C. E. Neal and H. E. Calbert (*J. Dairy Sci.*, 1955, **38** [6], 629–633).—With the given simple routine test, based on the inhibition by antibiotics of the reduction of 2:3:5-triphenyltetrazolium chloride (**I**) to a coloured formazan by metabolising bacteria, the following concn. of antibiotics could be detected in 1 ml of raw milk: penicillin 0·04, 0·3 unit; chlortetracycline 0·2, 0·3 μg; oxytetracycline 0·25, 1·0 μg; streptomycin 4·0, 0·6 μg. The first figure is the concn. detectable with *Streptococcus thermophilus* and the second with a commercial lactic starter as test organism. *Procedure*—Pasteurise 9-ml amounts of raw milk, controls and standards containing antibiotics at 80° C for 5 min. Rapidly cool to < 37° C, add 1 ml of inoculum [a diluted (1:1) 12 to 14-hr. culture of test organism in reconstituted sterile skim milk] to each tube, close with sterile rubber stoppers, invert each tube twice and incubate for 2 hr. in a water bath at 37° C. Add 0·3 ml of 4 per cent. aq. **I** (store this reagent at 7° C) to each tube, invert twice and heat at 37° C for 30 min. In the presence of inhibitory substances, samples remain white or are less pink than the control tubes. W. H. C. Shaw

3204. **The standard plate-count of milk as affected by the temperature of incubation.** F. J. Babel, E. B. Collins, J. C. Olson, I. I. Peters, G. H. Watrous and M. L. Speck (*J. Dairy Sci.*, 1955, **38** [5], 499–503).—In a detailed collaborative investigation the effects of varying temp. of incubation between 10° C and 45° C for periods of 1 to 10 days are studied in relation to the bacterial count obtained on 78 samples of raw and pasteurised milk. The mean results obtained under each of the selected conditions are detailed, and it is concluded that, with raw milk and an incubation period of 2 days, temp. of 26° C and 32° C give results of the same magnitude. With pasteurised milk the highest count is obtained at 32° C, and this temp. is recommended for both types of milk. Incubation at 37° C should be discontinued. W. H. C. Shaw

3205. **Colorimetric methods for studying the fermentation process in black-tea manufacture.** J. R. Todd (*Chem. & Ind.*, 1955, [25], 704–705).—The u.v. absorption spectra of aq. extracts of tea at different stages of fermentation, and of an aq. solution of a mixture of polyphenols (mainly catechins and their galloyl esters) isolated from green tea-leaf, gave almost identical curves, with a very strong absorption max. at 205 mμ. Values of absorption at 205 mμ were then obtained and compared with total oxidisable matter at various stages, and found to be in highly significant correlation. This therefore appears to be a convenient and rapid method of estimating polyphenols in tea. The colour intensity of tea extracts measured on a Unicam G.P. colorimeter with a blue filter (Ilford 303) showed a similarly close correlation with the decrease in initial total oxidisable matter, and colour development can therefore also be used, on a quant. basis, to follow the fermentation reaction.
S.C.I. Abstr.

3206. **Estimation of the proportions of coffee and chicory in mixtures.** Laboratories of J. Lyons & Co., Ltd. (*Chem. & Ind.*, 1955, [20], 549).—Because of the different characters of coffee and of chicory now in general use, the standard values formerly used for the sp. gr. of 5 per cent. w/v extracts in the determination of the composition of coffee and chicory mixtures (Hughes and Wise, *J. Soc. Chem. Ind., Lond.*, 1934, **53**, 189T) have been amended to 1·0064 and 1·0154 for coffee and chicory, respectively. These values correspond to 1·6 and 3·85 per cent., respectively, for the total solids contents of the extracts. S.C.I. Abstr.

3207. **Determination of carbon dioxide in beer.** S. Berntsson (*J. Inst. Brewing*, 1955, **61** [3], 229–230).—In the following titrimetric method, an excess of 18 *N* NaOH soln. (usually ≃ 8 ml per 350 ml of beer) is added to the beer in the bottle, which has previously been cooled at ≃ 0° C for ≮ 1 hr. The bottle is stoppered and the contents are mixed and, after weighing, 5 ml of the mixture are added to 200 ml of $CO_2$-free water, and titrated with 0·1 *N* HCl in the presence of phenolphthalein

until the colour changes from yellow - pink to yellow. After the addition of a known excess ($\simeq$ 15 ml) of 0·1 *N* HCl, the soln. is boiled for $\simeq$ 5 min. to expel the $CO_2$, cooled, and titrated with 0·1 *N* NaOH to a yellow - pink colour. The amount of alkali required should be $\not<$ 5 ml. A simple calculation based on the wt. of the beer and the difference between the excess of 0·1 *N* HCl added and the final back-titration gives the percentage of $CO_2$ with an error of $\not>$ 5 per cent. P. S. ARUP

3208. **Rapid determination of the bitter substances in hops and beer.** W. J. Klopper (*Brauwissenschaft*, 1955, **8** [5], 101–104).—The humulone-like substances in hops were determined in 18 samples by a modified spectrophotometric method, the analysis of a sample being made in 20 min. The sample of hops (5 g) is placed in 150 ml of benzene in a "Turmix" mixer and macerated by shaking at high speed for 1 min. It is filtered on a glass filter into a 250-ml calibrated flask and the hops on the filter are washed six times with 15 ml of benzene, the washings being collected in the calibrated flask and the vol. made up to 250 ml with benzene. After being shaken well, 1 ml of benzene extract is transferred by pipette into a 100-ml calibrated flask, 1 ml of 0·2 *N* NaOH soln. is added and the vol. is made up to 100 ml with methanol. Extinction in the spectrophotometer is read at 275, 325 and 355 m$\mu$ and the content of humulone-like substances is calculated. Results compared with those obtained by the polarimetric method of Govaert and Verzele indicated no variations $>$ 10 per cent. The spectrophotometric method of determinating *iso*-humulone in beer was carried out in 15 min. There was good agreement between taste trials (69 persons) of the bitter principles and the *iso*humulone content of some beers. S.C.I. ABSTR.

3209. **The chromatographic separation and identification of organic acids and their application to yeast.** J. N. Ladd and P. M. Nossal (*Austr. J. Exp. Biol.*, 1954, **32** [4], 523).—The authors use a modification of the method of Marshall, Donaldson and Friedberg (*Brit. Abstr. C*, 1952, 386). A column of silica gel is used for preliminary separation, with a solvent of gradually increasing polarity; final identification is achieved by two-dimensional paper-chromatography. By this procedure nine organic acids of biological interest have been completely separated and the position of eight others established. Except for the keto acids, the recovery is 95 to 102 per cent. Eight acids were found in yeast, of which five were identified as fumaric, succinic, α-oxoglutaric, malic and citric acids; the identity of the remaining three could not be established. The greatest variation in acid content between different batches of yeast was shown by succinic acid.
E. KAWERAU

3210. **The polarographic estimation of copper in fermented and unfermented liquors.** H. Tanner and H. Rentschler (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [2], 209–219).—The use of ethylenediamine as a supporting electrolyte improves the curves obtained in the polarographic estimation of copper. *Procedure*—Evaporate 10 ml of juice or 20 ml of wine in a platinum dish on a water bath, and then ash carefully. Dissolve the ash in 3 ml of conc. HCl, again evaporate and then heat for 3 hr. at 300° C. Dissolve the residue in 1 ml of *N* HCl and wash into a 10-ml flask. Make neutral to phenolphthalein with *N* aq. $NH_3$. Add 2 ml of the electrolyte soln. (240 g of ethylenediamine and 107 g of $NH_4Cl$ in 1 litre of $H_2O$) and make up to the mark. Take 5 ml for the determination with the polarograph; $E_{\frac{1}{2}}$ *vs.* the S.C.E. = − 0·54 V. It was found that grape musts contained 3 to 6 mg of copper per litre. Recoveries of added copper varied between 97·5 and 103·5 per cent. W. H. PARR

3211. **The identification of gluconic acid in wine made from grapes attacked by a fungus.** H. Rentschler and H. Tanner (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [2], 200–208).—The presence of gluconic acid, up to 2 g per litre, has been confirmed by paper chromatography in wines and musts prepared from grapes affected by *Botrytis cinerea*. Chromatograms of conc. extracts of the organic acids were run for 60 hr. with 5 *M* formic acid and pentanol (1 + 1) as solvent. The gluconic acid showed an $R_F$ value of 0·02 and was identified as its phenylhydrazone. Further chromatograms run with *n*-butanol - acetic acid - water (4 + 1 + 5) and developed with a soln. of 0·15 g of *o*-aminophenol in 20 ml of ethanol, mixed with 10 ml of 50 per cent. $H_3PO_4$, showed the presence of up to 100 mg per litre of glucuronic acid ($R_F$ = 0·33) and of galacturonic acid ($R_F$ = 0·16). Galacturonic acid appears to be a usual constituent of grape musts and wine. W. H. PARR

3212. **The estimation of iodine values.** H. Stähli (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [2], 121–162).—The methods of Hanus, Kaufmann and Wijs are compared. Results obtained by the Hanus method are considered to be less reliable than those by the Wijs method, since substitution appears to occur. The Wijs method gave even better results when the reagent was prepared so as to contain an excess of 7 g of iodine per litre.
W. H. PARR

3213. **Determination of oxygenated [epoxy] acids in fat.** N. S. Drozdov and N. P. Materanskaya (*Myasnaya Ind.*, 1954, **25** [3], 50). The method is based on the reaction

$$\text{·CH(O)CH·} + \text{HCl (dry)} \rightleftharpoons \text{·CH(OH)·CH(Cl)·}$$

A 0·2 *N* HCl soln. in ether is made by drying ether with $CaCl_2$ and then with Na and passing in dry HCl. Weigh a 0·4 to 0·8-g sample of fatty acids or a 0·8 to 1·0-g sample of fat into a 250-ml flask, add 5 ml of anhydrous ether and 15 ml of 0·2 *N* HCl soln. in anhydrous ether, let stand for 3 hr. at room temp., add 25 ml of neutral 96 per cent. ethanol and 0·5 ml of phenolphthalein soln. and titrate the residual HCl with 0·1 *N* aq. NaOH. Carry out a blank with the reagents. Oxygenated acids (per cent.) = $[B - (A - D) \times 0{\cdot}1 \times 0{\cdot}016 \times 100]$/wt. of sample (grams), where *A* is ml of 0·1 *N* NaOH used in titrating the test material, *B* is ml of 0·1 *N* NaOH used for the blank, and *D* is ml of 0·1 *N* NaOH required to neutralise the acidity of the original sample. CHEM. ABSTR.

3214. **An oxidation - adsorption method for the estimation of trisaturated glycerides.** G. Lakshminarayana and D. Rebello (*J. Sci. Ind. Res., B, India*, 1955, **14** [4], 189–190).—A modification of the acetone - permanganate method of Hilditch (*J. Chem. Soc.*, 1927, 3106) for the estimation of trisaturated glycerides is described which is designed to eliminate the carbonate-washing procedure and remove the azelao-glycerides by adsorption on a column of alumina. *Procedure*—An acetone solution of the fat is oxidised with permanganate until the purple colour persists for about 30 min. after the addition. The oxidation products, after

removal of acetone and subsequent treatment with $NaHSO_3$ and $H_2SO_4$, are extracted with light petroleum (boiling range 67° to 69° C) and the extract is washed twice with 10 per cent. $KHCO_3$ solution and water alternately. The washing is continued with dilute $H_2SO_4$ and again with water, until the extract is free of mineral acid. The light-petroleum extract, after removal of solvent, is dissolved in ether or chloroform and passed through a column of alumina (column diam., 18·5 mm). The alumina used was activated at 320° C for 1 hr. and packed wet, with light petroleum, and subsequently treated with ether. Azelao-glycerides are preferentially adsorbed by the alumina and the neutral glycerides and unsaponifiable matter are washed down with additional amounts of the eluting solvent. Definite fractions of the filtrate are collected and the amount of fat in each is determined. The fat obtained from the filtrate fractions is slightly acid. The amount of acidic product, calculated as azelaodistearin, is obtained by determining the acid value of the fat in each fraction. After determination of the acid value, the fat fractions are pooled and extracted with light petroleum. The extract is washed with water to remove the final traces of azelao-glycerides. G. C. JONES

3215. **Comments on the determination of vitamin A in natural products and especially cod-liver oils.** R. A. Morton and F. Bro-Rasmussen (*Analyst*, 1955, **80**, 410–418).—The analytical procedures of the B.P. and U.S.P. for the determination of vitamin A are discussed in relation to the newer problems arising out of the presence of three vitamin-A-active substances, *viz*, all-*trans* vitamin $A_1$, neovitamin $A_1$ and vitamin $A_2$, in fish-liver oils. These procedures are very suitable for products containing synthetic all-*trans* vitamin A, but are less precise for those containing mammalian liver oils or concentrates. Their application to the determination of vitamin A in cod-liver oil, for example, is an officially sanctioned convention giving a serviceable approximation. The nature of this approximation is discussed and it is shown that application of the Morton - Stubbs correction to the absorption graph of a natural oil tends to eliminate the vitamin $A_2$ and to over-correct for neovitamin $A_1$. This over-correction is balanced by the lower potency of the neovitamin, so that the B.P. and U.S.P. procedures yield a fair estimate of the vitamin-$A_1$ potency. The properties, biological potency and absorption spectra of the three active substances are discussed, with special reference to conversion factors. Liver oils from salt-water fish have at least 90 per cent. of their total activity supplied by vitamin $A_1$. A. O. JONES

3216. **Chromatographic separation of vitamin-A-active compounds in cod-liver oil.** F. Bro-Rasmussen, W. Hjarde and O. Porotnikoff (*Analyst*, 1955, **80**, 418–428).—A method is given for the chromatographic separation of neovitamin $A_1$, all-*trans* vitamin $A_1$ and vitamin $A_2$ in fish-liver oils. The adsorbent is calcium hydrogen orthophosphate activated by the method of Moore (*Ind. Eng. Chem., Anal.*, 1942, **14**, 707). The column is 300 to 600 mm long and the eluent is a mixture of light petroleum (b.p. < 70° C) with peroxide-free ether. The preliminary saponification and extraction are carried out as previously described (Hjarde, *Brit. Abstr. C*, 1951, 100). Absorption curves are given for the three active substances. In an example with the unsaponifiable fraction of cod-liver oil, with a 500-mm × 30-mm column, a light petroleum - ether eluent (16 + 1, v/v) and collection of 15-ml fractions, the fractionation graph (extinction at 325 mμ against vol. of eluate) showed three peaks, corresponding, respectively, with neovitamin $A_1$, all-*trans* vitamin $A_1$ and vitamin $A_2$. In another expt. the total vitamin-A-active compounds were extracted on a 100-mm column and the extract was treated on a 600-cm × 15-mm column with 400 ml of light petroleum - ether eluent (16 + 1, v/v) and then with 400 ml of a (12 + 1) mixture, 10-ml fractions being collected. The fractionation graph again showed the presence of the three active compounds with light absorption at 325 mμ. Good agreement was obtained between the determined content of the three compounds and the light absorption for the total vitamin-A fraction obtained by a normal chromatographic isolation of vitamin A.

A. O. JONES

3217. **A modified method for the spectrophotometric determination of vitamin A in margarine.** J. W. Lord and P. M. Bradley (*Analyst*, 1955, **80**, 429–438).—A method similar in principle to the official method (Statutory Instrument 1954, No. 613), but with de-fatted bone meal as the adsorbent, is described for the determination of vitamin A in margarine. *Procedure*—The unsaponifiable fraction from 10 g of margarine, prepared as in the official method, is transferred to a column of bone meal (22 to 25 cm × 1 cm) with light petroleum (boiling range 80° to 100° C). The column is washed with light petroleum until no more carotene or dye appears in the eluate. It is then eluted with light petroleum containing 16 per cent. v/v of peroxide-free ether, the eluate being collected in 5-ml fractions. The fractions containing vitamin A are identified by testing portions with Carr - Price reagent, and 2- or 3-ml aliquots of fractions answering to the test are combined and adjusted to a suitable vol. with light petroleum. The optical density is read at 315, 325 and 335 mμ and the difference between the observed densities at 315 and 335 mμ is deducted from the observed reading at 325 mμ to obtain the corrected optical density, which is then calculated to vitamin-A potency (i.u. per g) by means of the conversion factor 1830. For practical purposes, results are in good agreement with those of the official method. The bone meal should pass a No. 80 and be retained on a No. 170 B.S. sieve and the column may be used two or three times *in situ*. It is regenerated by washing by decantation with a mixture of light petroleum, ether and acetone (3 + 1 + 1), drying and screening. The main advantage of the method is the use made of a commercially available adsorbent that is more stable than the alkaline alumina of the official method.

A. O. JONES

3218. **Spectrophotometric and colorimetric determination of vitamin A by means of perchloric acid.** F. Čůta and J. Čelikovský (*Chem. Listy*, 1954, **48** [9], 1346–1350).—The fairly stable blue coloration of absorption max. at 543 mμ, formed when an approx. 60 per cent. soln. of $HClO_4$ is added to a chloroform soln. of vitamin A, is used as the basis of a simple spectrophotometric and colorimetric determination of the vitamin. The turbidity formed on the addition of the reagent is removed by centrifuging. For the colorimetric determination, an artificial standard is prepared of chlorophenol red in a phosphate buffer of pH 6·4, with an absorption max. at 575 mμ. Vitamin D does not interfere.

G. GLASER

3219. **Bound form of ascorbic acid. VIII. Determination of the bound form of ascorbic acid in ascorbigen.** V. Šanda and Ž. Procházka (*Českosl. Farmac.*, 1955, **4** [2], 63–64).—The acid hydrolysis of ascorbigen, which was found to release ascorbic acid, was investigated, the liberated acid being titrated with 2:6-dichlorophenolindophenol. The hydrolyses were carried out in a current of $CO_2$ or N. The reaction was found to be more complex than unimolecular. In all cases, except with HCl, the amount of ascorbic acid released reached, and remained at, a maximum. A table of the times taken for this is given, and the course of the hydrolysis is plotted. With HCl, the ascorbic acid content fell after the maximum, owing to slow decomposition. A further disadvantage of HCl was the reddening of the hydrolysed solution. Sulphuric acid (1 per cent.) was found most suitable for hydrolysing concentrates. For fresh plant juices, 3 g of $HPO_3$ + 8 ml of glacial acetic acid in 100 ml of $H_2O$ was best, as it effected the smooth decomposition of the complex compounds and stabilised the ascorbic acid formed. The method was applied to a number of plants and the results are tabulated. A. O. Jakubovic

See also Abstract 2932.

## Sanitation

3220. **A sampling technique for small air-borne particles. Particle-size distribution by combined use of light and electron microscopes.** J. D. Wilcox and W. R. van Antwerp (*Arch. Ind. Hlth*, 1955, **11** [5], 422–424).—A combined light and electron particle-size analysis technique, which is particularly suited to heterogeneous air-borne samples, is described. The sampling technique consists in depositing the particulate material directly on to an electron-microscope specimen film supported on a 200- (or 400-) mesh screen, which is mounted in the supporting cap used in the electron microscope. A five-stage cascade impactor (Wilcox, *Arch. Ind. Hyg.*, 1953, **7**, 376) is used to obtain a partially size-graded sample. The individual jets yield size-graded sample fractions that fall readily within a 1 to 100-$\mu$ range for the electron-microscope analysis. Special slides and screws are used in the cascade impactor. I. Jones

3221. **Determination of quartz of various particle sizes in quartz - silicate mixtures [in dusty air].** C. M. Jephcott and H. F. V. Wall (*Arch. Ind. Hlth*, 1955, **11** [5], 425, 430).—The phosphoric acid method (Talvitie, *Brit. Abstr. C*, 1951, 469) for the determination of quartz in the presence of silicates is modified to give a simple and rapid procedure which is applicable to a wide variety of siliceous materials. When 0·25-g samples are used and the decomposition is carried out at 230° to 240° C for $\simeq$ 15 min., no ppt. is formed on dilution. Quartz can be estimated in coarse and fine dusts by the method given with an absolute error of $< \pm$ 1 per cent. I. Jones

3222. **Determination of hydrogen sulphide in the atmosphere.** W. Lang and E. Mader (*Z. anal. Chem.*, 1955, **145** [3], 179–184).—Hydrogen sulphide (10 to 30 $\mu$g) may be determined by absorption in dil. starch - iodide soln. and calculating the amount of $H_2S$ colorimetrically by measuring the decrease in extinction, or by titrating the excess of iodine with $Na_2S_2O_3$. Alternatively, the gas may be absorbed in cadmium acetate soln.; the cadmium sulphide is oxidised with iodine and hydrochloric acid and the excess of iodine is titrated with $Na_2S_2O_3$. By titration, 10 to 30 $\mu$g of gas can be determined with an accuracy of $\pm$ 5 per cent. P. Haas

3223. **Determination of low alkalinity or acidity in water.** T. E. Larson and L. Henley (*Anal. Chem.*, 1955, **27** [5], 851–852).—The sample (200 ml) is treated with successive small additions of 0·02 *N* $H_2SO_4$ and the pH is measured at each stage, after aeration, at constant temp. Extrapolation of the almost linear curve of $[H^+]$ against ml of $H_2SO_4$ to zero or to $1 \times 10^{-7}$ gives the $H^+$ concn. of the sample. A sensitivity and accuracy of $\pm$ 0·05 p.p.m. of $CaCO_3$ is given. D. A. Pantony

3224. **Determination of alkalinity and total cations in water.** B. A. Sard and J. Ungar (*Chem. & Ind.*, 1955, [25], 699–700).—Alkalinity is determined by titration with 0·1 to 0·02 *N* HCl or $HNO_3$, methyl orange screened with xylene cyanol FF being used as indicator. The sample is then passed through Zeo-Karb 225 cation-exchange resin (14/52 B.S. mesh) at a rate of 5 ml per min., the first 50 ml of eluate being discarded. A 100-ml aliquot is then titrated with 0·02 *N* NaOH solution and the equiv. mineral acidity is calculated. The total cation content is obtained by adding the results of the two titrations, and the content of Na may be obtained by subtracting the total hardness figure from it. Typical results obtained (in p.p.m. of $CaCO_3$) show good agreement with those from conventional methods. S.C.I. Abstr.

3225. **The determination of substances in minute quantity. X. Colorimetric determination of sodium in water.** T. Kato, Y. Okinaka and T. Nomura (*Technol. Rep. Tohoku Univ.*, 1954, **19** [1], 81–84).—The method consists in pptg. the sodium as sodium magnesium uranyl acetate, dissolving the ppt. in hot water and determining the magnesium with 0·1 per cent. Titan yellow. A Duboscq-type colorimeter is used. Potassium chloride interferes but ammonium sulphate, calcium nitrate and ferric alum do not. R. J. Magee

3226. **Spectrophotometric technique for calcium [in water].** L. Aconsky and M. Mori (*Anal. Chem.*, 1955, **27** [6], 1001).—A method is described for determining the concn. of Ca in water, based on the titration of the sample with EDTA (disodium salt), with murexide as indicator. The colour change is from pink to lavender; the end-point is not sharp by visual techniques, but the use of a spectrophotometer enables a sharp end-point to be detected. The technique is rapid, and one titration can be completed in about 3 min. with a 10-ml sample. A. J. Mee

3227. **Flame-photometric determination of calcium in sea water and marine organisms.** T. J. Chow and T. G. Thompson (*Anal. Chem.*, 1955, **27** [6], 910–913).—A direct flame-photometric procedure is described. The extent of band-width interference caused by the major constituents of sea water ($Cl'$, $Na^+$, $SO_4''$, $Mg^{++}$, $K^+$ and $Sr^{++}$) was studied and, at 422·7 m$\mu$, the spectral line chosen for the calcium-emission intensity measurement, none of these ions emitted an appreciable amount of light. The negative radiation interference caused by $K^+$, $Mg^{++}$, $Cl'$ and $SO_4''$, and the positive interference of $Na^+$, were also studied. An "internal standards" technique was used to eliminate the effect of the interfering elements. Samples of fresh and sea water gave results in good agreement with those of previous workers. A. J. Mee

3228. **Determination of iodine in natural waters (sodium chloride as a reagent in the catalytic reduction of ceric ions).** M. Dubravčić (*Analyst*, 1955, **80**, 295–300).—By the method presented, I can be determined in a 14-ml sample of water, with an error $< \pm 0{\cdot}3$ $\mu$g per litre, by means of its catalytic effect on the reduction of $Ce^{IV}$ salts by $As_2O_3$. The reagents, apparatus and technique are those formerly described (Rogina *et al.*, *Anal. Abstr.*, 1954, **1**, 87; Dubravčić, *Ibid.*, 1955, **2**, 1526). Standard water used for the preparation of calibration graphs and reference standards must contain $< 0{\cdot}3$ $\mu$g of I per litre, and may be prepared by distillation from NaOH. The reaction mixture (10 ml) should contain 7 ml of sample water, 1 ml of 20 per cent. w/v NaCl soln., 0·5 ml of 0·1 *N* $As_2O_3$, 0·5 ml of 60 per cent. w/v $H_2SO_4$ and 1 ml of 0·02 *N* $Ce(SO_4)_2.2(NH_4)_2SO_4.4H_2O$. To prepare the calibration graph, the necessary amounts of standard KI soln. are diluted with standard water to 7 ml. The test without $As_2O_3$ is made simultaneously with the determination of I. One tube (*A*) contains 7·5 ml of dist. water, 1 ml of the NaCl soln. and 0·5 ml of the $H_2SO_4$. Another tube (*B*) contains 7 ml of the sample, 0·5 ml of dist. water, 1 ml of the NaCl soln. and 0·5 ml of the $H_2SO_4$. The tubes are treated in the same manner as those to which $As_2O_3$ has been added. The difference in extinction values for the tubes ($B - A$) is subtracted from the extinction value determined for the sample by the ordinary procedure, and the amount of I is ascertained from the calibration graph. A. O. Jones

3229. **New method for detection of coliform organisms.** A. A. Hajna and S. R. Damon (*J. Amer. Wat. Wks Ass.*, 1955, **47** [6], 631–636).—Buffered deoxycholate glucose broth (**I**) is proposed as a presumptive medium to replace standard lactose broth in the primary inoculation of samples of water and food. A new procedure is described for determining the density of coliform bacteria in samples by transfer from **I** to buffered deoxycholate lactose broth as a confirmatory medium. Details of a very large number of tests comparing the new with the standard method are reported, and it is claimed that more positively confirmed findings were obtained with the new method. S.C.I. Abstr.

3230. **Analytical determination of trace constituents in metal-finishing effluents. VI. The colorimetric determination of chromium in effluents.** E. J. Serfass, R. F. Muraca and D. G. Gardner (*Plating*, 1955, **42** [1], 64–68).—Colorimetric procedures for the determination of the sexavalent and total chromium content of effluents in the range 5 to 50 p.p.m. are presented. In the method for total chromium, a preliminary fuming with nitric and sulphuric acids is carried out to decompose organic material. Insoluble substances remaining after dilution with water are filtered off. Iron, vanadium and molybdenum are extracted as the cupferrides from a portion of the filtrate. The soln. is then oxidised with ammonium persulphate in the presence of Ag as catalyst, and $KMnO_4$ is added to ensure the complete oxidation of Cr to the sexavalent state. The permanganate colour is destroyed by boiling with HCl; on adding *sym*-diphenylcarbazide (**I**) a red - violet colour is formed, whose intensity is measured at 540 m$\mu$. The colour is stable for at least 2 hr. For sexavalent Cr, the acidity of the sample is adjusted to 0·2 *N* with $H_2SO_4$, **I** is added and the colour is measured as before. Errors may be caused if materials that can be oxidised by $Cr^{\cdots\cdots}$ are present, *e.g.*, cyanides, or if the $Cr^{VI}$ is not present in a form suitable for reaction with **I**. Good results were obtained for 5 to 50 p.p.m. of Cr in soln. containing 5000 p.p.m. of each of the following ions in simultaneous admixture: $Ag^{\cdot}$, $Hg^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $As^{\cdot\cdot\cdot\cdot\cdot}$, $Sb^{\cdot\cdot\cdot\cdot\cdot}$, $Sn^{\cdot\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$ and $PO_4'''$. The limit of detection is 1 p.p.m. of Cr. N. E.

3231. **Analytical determination of trace constituents in metal-finishing effluents. VIII. The colorimetric determination of ammonia in effluents.** E. J. Serfass and R. F. Muraca (*Plating*, 1955, **42** [3], 265–266).—The ammonia is distilled with sodium hydroxide and sodium sulphide into 0·1 *N* HCl, and the ammonium content of the distillate is determined by Nessler's reagent. The limit of detection is 50 $\mu$g of $NH_4^{\cdot}$ or 0·5 p.p.m. **IX. The determination of free chlorine in effluents.** E. J. Serfass, R. F. Muraca and D. G. Gardner (*Ibid.*, 1955, **42** [3], 401–402). The *o*-tolidine reaction is used. The presence of $Fe^{\cdot\cdot\cdot}$ and $Mn^{\cdot\cdot\cdot}$, oxidising agents and nitrites affects the results, but not 1 p.p.m. of Zn, As, Sb, Bi, Ni, Cu, $PO_4'''$, Cd, $Cr^{\cdot\cdot\cdot}$, Co, Pb, Ba, Ag and Hg, or 20 p.p.m. of Na, K, Ca, Mg, Al, Cl′, $NO_3'$ and $SO_4''$. The limit of detection is 25 $\mu$g of Cl. N. E.

See also Abstracts 3002, 3081.

## Agriculture and Plant Biochemistry

3232. **Characterisation and determination of flavone derivatives.** M. R. Paris and J. Cornilleau (*Ann. Pharm. Franç.*, 1955, **13** [3], 192–199).—The colour reactions given by flavones, flavonols, flavanones, chalkones and *iso*flavones, arising both from the nucleus and from the phenolic functions, are reviewed and their specificity is discussed. For quant. purposes the cyanidine reaction (with nascent H from Mg and HCl) is preferred for flavones, flavonols and flavanones. Owing to the different colours produced, different standards are used: luteoline for flavones, rutoside for flavonols, and hesperidoside for flavanones. *Procedure*—A solution (1 to 4 ml) containing 1 to 4 mg of flavone derivative is mixed with 3 ml of 15 per cent. $AlCl_3$ and 0·5 ml of 20 per cent. aq. $NH_3$ soln., then made up to 10 ml and centrifuged. The ppt. is washed with dil. $NH_3$ soln., re-centrifuged and dissolved in 2 ml of HCl (22° Bé) and, after 10 min., made up to 5 ml. Magnesium (75 mg) is then added and the absorption is measured after 15 min. at 500 or 530 m$\mu$, according to the derivative being determined. E. J. H. Birch

3233. **Quercetin glycosides of Grimes Golden apple skin.** [**Separation and identification.**] H. W. Siegelman (*J. Biol. Chem.*, 1955, **213** [2], 647–654).—A method for the paper-chromatographic separation and identification of a mixture of quercetin and quercetin glycosides is described. The method is applied to extracts of apple skin. After repeated chromatography each product is hydrolysed by 2 *N* $H_2SO_4$ at 100°C, and the aglycone portion is identified by its $R_F$ value in various solvents and by colour reactions. The sugar component is identified by paper chromatography. J. N. Ashley

3234. **Determination of chlorogenic acid in plant material.** K. Paech and H. Ruckenbrod (*Ber. disch. bot. Ges.*, 1953, **66**, 76–79).—If the material to be extracted contains a polyphenol oxidase, it is first heated at 100° C for 1 hr. or immersed in 1 per cent. $NaHSO_3$. It is then ground in quartz sand and extracted (× 3) with 70 per cent. ethanol (total vol. ≃ 10 times that of the starting material). The extract is evaporated *in vacuo* at 40° to 50° C to about one-tenth of its original vol. For chromatographic separation, 0·01 ml is placed on Whatman filter-paper No. 1, and the paper is developed overnight at 20° C in the aqueous phase of butanol - methanol - water (4 : 1 : 5). The next day the paper is subjected for 8 hr. to the descending butanol phase. Chlorogenic acid (**I**) prepared according to Freudenberg's method (*Chem. Abstr.*, 1920, **14**, 2639) can be used as a standard. After being dried, **I** shows a dull-blue fluorescence at an $R_F$ value of 0·73 in u.v. light, which becomes greenish yellow when moistened with aq. $NH_3$ soln. When sprayed with Höffner's reagent (**II**) (1 per cent. of $NaNO_2$ in 1 per cent. methanol) the spot becomes yellow, changing to red when sprayed with *N* NaOH. Caffeic acid gives a blue fluorescence (with $NH_3$ a brighter blue) at an $R_F$ value of 0·83, and with **II** a brownish-red spot. Quinic acid has an $R_F$ value of 0·34, and the spot becomes visible after spraying with bromophenol blue. **I** can be eluted from the paper and determined quant. spectrophotometrically, either with or without previous treatment with **II** and NaOH. CHEM. ABSTR.

3235. **A method for the determination of total sulphur in soils.** A. Steinbergs (*Analyst*, 1955, **80**, 457–461).—A rapid method has been developed for the turbidimetric determination of S in small samples of soil. *Procedure*—The air-dry soil (0·5 g) is fused in a nickel crucible with 1·4 g of $Na_2O_2$, at ≃ 800° C for 5 to 7 min. The sulphate is determined turbidimetrically after interfering ions have been removed. A reagent blank is prepared, either by fusing 0·5 g of purified quartz with $Na_2O_2$, or by dissolving the $Na_2O_2$ in water. Reproducible turbidity readings are obtained by using a "seeded" $BaCl_2$ suspension, the preparation of which is described. The method has been applied to various soil types ranging in total sulphur content from 0·002 to 0·078 per cent. A. O. JONES

3236. **Separation and determination of acetic and lactic acids by paper partition chromatography and its application to silages.** Y. Birk and A. Bondi (*Analyst*, 1955, **80**, 454–457).—Spots of the ammonium salts of the acids are applied to two filter-papers. One filter-paper is immediately transferred to the chromatographic chamber and developed with *n*-butanol satd. with aq. $NH_3$; the other paper is kept at 26° to 30° C for 5 to 7 hr. to evaporate the ammonium salts of the volatile fatty acids, and then placed in the chamber and developed. The spots on the first paper give the volatile fatty acids and the sum of acetic and lactic acids; those on the second paper give lactic acid alone. The spots are indicated by spraying with methyl red - thymol blue in formaldehyde soln. at pH 5·2 and exposing to $NH_3$ vapour. In the application of the method of silage, the sample (100 g) is extracted with 500 ml of water and 10-$\mu$l aliquots are chromatographed. Solutions of pure acetic, lactic and butyric acids serve as standards yielding spot areas of about 500 sq. mm. A. O. JONES

3237. **Detection and determination of insecticide E605 in forensic chemistry.** J. Derkosch and F. X. Mayer (*Mikrochim. Acta*, 1955, [2-3], 495–504).—Insecticides based on the esters of thiophosphoric acid (the dimethyl ester, E605-parathion, and the diethyl ester, E605-Staub) are readily separated from biological material by steam-distillation and ether extraction of the distillate. The ester is determined by measuring the u.v. absorption of solutions of the residue in ethanol. Computational elimination of the interfering materials is easier at low concn. of ester. Measurements of the i.r. absorption permit identification of the ester (methyl or ethyl) if present at sufficiently high concn.
D. R. GLASSON

3238. **The identification of E605 (parathion).** W. Paulus, H. J. Mallach and U. Janitzki (*Arzneimittel-Forsch.*, 1955, **5** [4], 241–244).—The method of Averell and Norris (*Brit. Abstr. C*, 1949, 170) was studied and modified. Details suitable for quant. determination are given. The nitro group is reduced with zinc in HCl solution, the amine so formed is diazotised, coupled with N-naphthylethylenediamine, and the colour estimated photometrically. Quantities from 29 to 260 $\mu$g of parathion can be estimated with an accuracy of ± 18 $\mu$g. To correct for interfering materials present in blood, a determination omitting the reduction step is performed. The method is suitable for forensic use, but as it is non-specific the phosphorus should also be determined by wet combustion and oxidation of the sample, followed by formation of molybdophosphoric acid and reduction to molybdenum blue. Details of a suitable method are given. The specificity is increased by a preliminary steam-distillation of the parathion from neutral solution. P. S. STROSS

3239. **The quantitative determination of indol-3-ylacetic acid by means of paper chromatography and paper electrophoresis.** R. Müller (*Beitr. Biol. Pflanz.*, 1953, **30**, 1–32).—Indol-3-ylacetic acid (**I**) can be chromatographed on paper in weakly basic solvent mixtures such as *n*-propanol - aq. $NH_3$ - $H_2O$, ethyl methyl ketone - pyridine - water or *n*-butanol - aq. $NH_3$ - $H_2O$; it can be qual. detected on the bands by means of the cinnamaldehyde - HCl colour test, the cress and the pea tests, or by exposure of the bands to light at a wavelength of 270 to 290 m$\mu$ and photoprinting on photographic paper. The cress test is well suited for quant. determination of the chromatographed **I**; the values are in good agreement with those obtained from extinction coefficients. **I** can be determined in urine by concentrating 2 litres of urine to 130 ml, allowing to stand overnight with 130 ml of peroxide-free ether, extracting twice more with 50-ml portions of ether and evaporating the combined ether soln. to dryness, when the **I** separates on rubbing the residue with 15 ml of hot water. The ether extract may also be evaporated to 1 ml and chromatographed on paper by the use of *n*-propanol - aq. $NH_3$ - $H_2O$ as solvent. **I** can be separated from maize by extraction with light petroleum, followed by extraction with ether for 8 hr., evaporation of the ether extract and chromatography of an aq. soln. of the residue. **I** isolated from these extracts showed $\lambda_{max.}$ 280 to 285 m$\mu$, with a minimum at 245 m$\mu$, and was present in maize to the extent of 0·1 $\mu$g per g. CHEM. ABSTR.

3240. **Determination of salts of ethylenebisdithiocarbamic acid in the presence of copper salts.** P. Fontana and R. Martelli (*Ann. Chim., Roma*, 1954, **44** [12], 978–981).—In the analysis of anticryptogam solutions containing copper salts and ethylenebisdithiocarbamic acid (**I**), the method of Clarke *et al.* (*Brit. Abstr. C*, 1952, 225) cannot be used owing to the influence of $Cu^{\cdot\cdot}$ on the acid decomp. of **I**. A modified procedure, with the same apparatus, is used in which the **I** is decomposed with $H_4Fe(CN)_6$, the Cu being converted into insoluble $Cu_2Fe(CN)_6$. The $CS_2$ evolved is washed through aq. Pb acetate (to remove $H_2S$ or $SO_2$ arising from impurities in the product), absorbed in methanolic KOH and titrated iodimetrically. Instead of $H_4Fe(CN)_6$, a mixture of $H_2SO_4$ and sufficient $K_4Fe(CN)_6$ to ppt. all the $Cu^{\cdot\cdot}$ may be used. L. A. O'NEILL

See also Abstracts 3120, 3253.

## 5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

### General

3241. **Continuous determination of oxygen in gases.** J. T. Corcoran (*Anal. Chem.*, 1955, **27** [6], 1018–1019).—Modifications in an apparatus due to Brady (*Brit. Abstr. C*, 1949, 203) are described. This method for the determination of oxygen in gases involves reaction between the oxygen in the sample and an alkaline solution of sodium anthraquinone-2-sulphonate, which is colourless when oxidised and red when reduced. A colorimeter is used to measure the absorbance of the partially oxidised reagent. A device is described to permit easy checking of the flow rate. Precision is increased to $\simeq$ 1 p.p.m. of oxygen in the range 0 to 60, and $\simeq$ 5 p.p.m. in the range 0 to 400. A. J. MEE

3242. **A magnetic method of moving the sample-boat in the direct determination of oxygen and in other micro-combustion methods.** W. Zimmermann (*Mikrochim. Acta*, 1955, [4], 888–895).—An arrangement for moving the platinum boat in a micro-combustion tube, by means of an iron guide fixed to the boat and controlled by two external magnets, is described and illustrated. The device is very useful, especially where a gas by-pass system is obligatory, whilst one serious source of error in the direct determination of oxygen, *viz*, influx of air, is eliminated. W. J. BAKER

3243. **Steam-distillation apparatus. I. Determination of nitrogen.** S. Tourlière (*Ind. Agr. Aliment.*, 1955, **72** [4], 259–265).—A steam-distillation apparatus utilises two concentric glass tubes of which the outer one functions as a steam jacket and forces steam through the bottom of the inner one, into which a micro-Kjeldahl digestion residue is introduced together with sufficient NaOH to liberate $NH_3$ completely. The entrained $NH_3$ passes through two bulbs, which are designed as condensate traps, and is then led through a water condenser into a flask containing 2 per cent. boric acid solution, of which aliquots are titrated with 0·05 or 0·01 *N* HCl (bromocresol green - methyl red indicator). S.C.I. ABSTR.

3244. **A rapid method for the determination of steam-volatile substances: nitrogen by the Kjeldahl method, ammonia, acetone bodies in blood, volatile fatty acids and mandelic acid.** V. Klingmüller, G. J. Erdmann-Müller, J.-G. Rausch-Stroomann and G. Brune (*Arzneimittel-Forsch.*, 1955, **5** [3], 105–109).—An all-glass apparatus, in which volatile substances can be conveniently steam-distilled, is described. A detailed account is given of its use in the micro-determination of nitrogen by the Kjeldahl method, the determination of acetone and α-hydroxybutyric acid in biological fluids, and the determination of volatile fatty acids. The determination of mandelic acid is also discussed. It is claimed that this type of apparatus increases the speed of these determinations. P. S. STROSS

3245. **Twenty-stage molecular distillation unit.** F. W. Melpolder, T. A. Washall and J. A. Alexander (*Anal. Chem.*, 1955, **27** [6], 974–977).—A 20-stage counter-current molecular still with a capacity of 1500 ml, and consisting of 1 large and 19 small still-pots connected in series, has been developed for the distillation of high-boiling samples, such as heavy petroleum products. The unit can be used as an equilibrium-type still for less than 260 ml and as a batch distillation unit for larger samples, and can be operated unattended. With a test mixture, an efficiency of 0·8 theoretical plate per stage was attained. K. A. PROCTOR

3246. **Ancillary equipment for the chromatography of phosphate esters.** G. R. Haney and T. C. Loughheed (*Chem. & Ind.*, 1955, [25], 702–703).—The location of phosphate esters on chromatograms is effected by spraying with molybdate reagent and irradiating with u.v. lamps to produce coloured spots. The colour intensity is increased if both sides of the paper are irradiated, and a simple design of an irradiation box containing four u.v. lamps, holding the chromatogram suspended on nylon mono-filament between pairs of lamps, is described. An automatic magnetic mechanism which, when left overnight, produces fully equilibrated and developed chromatograms, is also described. S.C.I. ABSTR.

3247. **A semi-micro dilution viscometer.** V. E. Hart (*J. Polym. Sci.*, 1955, **17** [84], 207–214).—An accurate semi-micro capillary viscometer is described in which dilutions can be made. A glass-valve assembly eliminates evaporation and makes operation convenient. Techniques for semi-micro work are described and specifications are given for an instrument suitable for intrinsic viscosity determinations with 1 ml of solution. N. E.

3248. **Instrument for measuring surface tensions and viscosities.** A. P. R. Pochan (Brit. Pat. 733,602, Date Appl. 19.11.53).—A transparent capillary tube is held vertically in a clamp so that its lower conical end coincides with the surface level of the liquid (of which the viscosity or surface tension is to be measured) held in a container. A syringe, connected to the upper end of the capillary tube, applies suction to make the liquid rise in the tube. If $h$ is the free height of the liquid in its position of equilibrium inside the capillary tube, $d$ is the sp. gr. of the liquid at the temp. of the determination, and $k$ is the constant for the particular tube (determined with a liquid of known properties), then the surface tension, $\gamma$, of the liquid in dynes per cm is given by $\gamma = khd$. The apparatus may also be used for determining viscosity from the time of flow down the tube of a column of liquid of known height. J. M. JACOBS

3249. **Method and apparatus for testing lubricants.** National Research Development Corp. (Inventors: F. T. Barwell and A. A. Milne) (Brit. Pat. 732,447, Date Appl. 16.5.52).—Mating surfaces in the form of cylinders set with their axes crossing are employed. The cylinders are moved relatively to one another by giving each a motion such that any point on either cylinder comes into contact only once with the point on the other; the cylinders are pressed together under a known force. The relative movement may be obtained by rotating one of the cylinders and translating the other, without rotating it, both in the direction of, and at right angles to, the axis of the rotating cylinder. Contact on the rotating cylinder then takes the form of a helix and, on the fixed cylinder, of a straight line. The force may remain constant, but will usually be increased progressively according to a known law. Thus the loading conditions are known, and from the examination of the traces on the cylinders the conditions under which scuffling began can be ascertained. J. M. JACOBS

3250. **Apparatus for measuring the moisture content of granular or powdered materials.** British Electrical & Allied Industries Research Assoc. (Inventor: P. G. Finn-Kelcey) (Brit. Pat. 731,826, Date Appl. 20.5.52).—The apparatus is based on the principle that a weighted body of suitable shape falling on to the surface of granular material will penetrate into the mass to an extent that varies with the percentage of moisture present in the material, since the friction between the body and the grains of material and that between individual grains decreases with decreasing moisture content of the material. The weighted body comprises a stainless-steel blade approx. 8 in. high, 3 in. wide and 1/16 in. thick, which is allowed to fall freely before penetrating into the mass of powder. J. M. JACOBS

3251. **A multiple automatic apparatus for the estimation of nicotine and tar in cigarette smoke.** C. Decker, A. Girardet, P. Golaz and R. Regamey (*Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** [2], 178–182).—The apparatus consists of a disc with five apertures, in each of which a cigarette is placed. The disc is rotated by a motor so that each aperture is connected in turn with a vacuum system, which draws the smoke through absorption towers containing 30 per cent. $H_2SO_4$ to absorb the nicotine and $CHCl_3$ to absorb the tar. Nicotine is estimated as the dipicrate, and the tar by evaporating the $CHCl_3$ and weighing the residue.
W. H. PARR

See also Abstracts 2947, 3086, 3195, 3220.

## Optical

3252. **A capillary photometer.** G. Gorbach (*Mikrochim. Acta*, 1955, [4], 879–881).—A capillary photometer suitable for micro-determinations of trace elements, compounds, etc., is described and illustrated. Capillary cells, 100 mm long by 3 mm wide, with a vol. of 0·7 ml, are used in the instrument. W. J. BAKER

3253. **Performance of interference filters in a simple flame photometer.** W. G. Schrenk and B. L. Glendening (*Anal. Chem.*, 1955, **27** [6], 1031–1033).—The performance of interference filters in a simple flame photometer for determining Na and K in plant tissue has been studied. Magnesium depressed the intensity of emission of Na and K, Na and Ca had only a slight effect on K, Ca enhanced the emission of Na, but the effect of K on Na was negligible. Standards containing Mg and Ca in quantities approximating to those present in plant tissue must be used if Na and K are to be determined accurately. For 16 samples of alfalfa, the standard deviation was 1·9 per cent. for Na and 2·24 per cent. for K.
K. A. PROCTOR

3254. **Optical systems for spectrochemical analysis.** Leeds & Northrup Co. (Brit. Pat. 731,943, Date Appl. 30.7.52).—An optical system is provided which, except for astigmatism, is free from off-axis aberrations. The mounting of the components is greatly simplified and there is no need for adjustment of the reflecting surfaces. A concave spherical mirror is supported in a housing secured to a tubular structure, with the axis of the mirror coincident with the longitudinal axis of the tube. Spectral dispersing means, *e.g.*, a plane reflection grating, is supported within the tube facing the mirror so that the centre of the dispersing element is intercepted by the longitudinal axis of the tube. By this arrangement, two areas of the mirror are symmetrically disposed with respect to the axis, to provide optical paths to the grating from focal points of the mirror symmetrically and laterally displaced from the longitudinal axis of the tube.
J. M. JACOBS

3255. **Multiple-slit spectrograph for direct-reading spectrographic analysis.** Leeds and Northrup Co. (Brit. Pat. 732,058, Date Appl. 28.7.52).—A single photomultiplier tube or other sensitive element is utilised in combination with a series of entrance and exit slits, each provided with independently operated shutters and means for scanning either the entrance or exit slits. The system may include two entrance slits and a number of exit slits prepared in a rotatable disc, which is provided with appropriate slots for each desired line of the analysis, the shutter action being brought about by rotation of the disc. J. M. JACOBS

3256. **The new universal emission quantometer and its application.** M. F. Hasler, E. Davidson, H. Orr and W. H. Barry (*Mikrochim. Acta*, 1955, [2–3], 596–609).—New 2-m and 1·5-m spectrometers are described. The position of the phototubes is much more flexible than in the older ARL model (1946), and the max. no. of phototubes can be 68 and 50 in the 2-m and 1·5-m instruments. Suitable dispersions of spectrum lines of 5·2 and 2·6 A per mm are given by the 2-m instrument over the ranges 1966 to 8750 A in the first order and $< 4375$ A in the second order, respectively; the 1·5-m instrument has a useful spectrum range of 1500 to 7600 A in the first order with dispersions of 6·9 and 3·5 A per mm. The use of a novel optical device to separate the P line at 2149·1 A from the Cu line at 2148·97 A is described for the determination of P in steel; seven samples ranging in phosphorus concn. from 0·013 to 0·02 per cent. gave results reproducible to about $\pm$ 0·002 per cent.
D. R. GLASSON

3257. **Investigation into the spectrochemical analysis of non-metals by low-tension electrical discharge.** K. Pfeilsticker (*Mikrochim. Acta*, 1955, [2–3], 358–375).—The spectrochemical detection of non-metals can be improved by the use of powerful low-tension discharge, and the sensitivity can be increased by lowering the self-induction. Details of a newly-designed vacuum chamber are given. Sulphur and halogens (except F) are detected in

quantities $< 1\ \mu g$; the F lines become visible at $10\ \mu g$. The presence of A in air is readily shown. The S is readily detected in noble metals attacked by it, and in steel at concn. $< 0{\cdot}02$ per cent. Earlier experiments prove that H in metals may be determined. The conditions are stated and the opposing demands of excitation and volatilisation are discussed. A short theoretical treatment of low-tension discharge includes a comparison of the spectral character (blackening difference) of spark discharges of durations from 1 to $3 \times 10^{-4}$ sec. for small to medium current strengths.

D. R. GLASSON

3258. **Spectrographic effects of variation of the discharge gas in carbon arcs and high-tension sparks.** A. Schöntag (*Mikrochim. Acta*, 1955, [2–3], 376–389).—A quartz cell is designed, for use with carbon electrodes, that permits work in a foreign gas with a normal support without significant delays. All cyanogen bands are avoided when working with nitrogen-free discharge gases. The intensities of spectral lines of various elements are appreciably dependent on the discharge gas, particularly of hydrogen additives; chemical reactions during the emission are thus significant. Accurate results are possible only if the influence of atm. moisture is eliminated or taken into account. The material disintegration in the carbon arc depends entirely on the chemical reactivity of the discharge gas or its elements, and not on the electrical energy transformed into heat. An a.c. arc can be burned in argon plus 10 per cent. of oxygen even when the purest carbon is used, if the current strength is $> 4$ amp. D. R. GLASSON

3259. **A new atomiser for a flame photometer.** H. Straubel (*Mikrochim. Acta*, 1955, [2–3], 329–335).—A new atomiser operating on an electrostatic principle, and requiring no compressed air, has been developed. In contrast to pneumatic atomisers hitherto in use, it is highly efficient, since the dispersed particles are guided into the flame by appropriate electrostatic fields. D. R. GLASSON

3260. **Double-beam [infra-red] spectrometers.** C. A. Parsons & Co., Ltd. (Inventor: J. C. O. Rochester) (Brit. Pat. 732,719, Date Appl. 10.9.52).—The advantages of low stray energy are secured while using a standard double-beam (in time) spectrometer, by a special rotating chopper disc, which interrupts the radiation at twice the frequency of the beam-switching device. This beam-switching device consists of two reciprocating mirrors inclined at a fixed angle to one another. The phase relation between the chopper disc and the mirrors is such that when the chopper begins (or ceases) to interrupt the radiation, the reciprocating mirrors are at the limit of their travel in each direction. J. M. JACOBS

3261. **A low-temperature microscope stage for metal specimens.** D. Hull and R. D. Garwood (*J. Sci. Instrum.*, 1955, **32** [6], 232–233).—A copper cooling rod projects below the microscope stage and dips into a refrigerant contained in a Dewar flask. The specimen is mounted in a slot cut in the upper face of the stage. The temp. of the specimen is measured by a thermocouple held in a plastic sleeve against the specimen by a small spring.

G. SKIRROW

## Electrical

3262. **Adaptation of the rectified radio-frequency method of chemical analysis for chromatographic zone location.** G. G. Blake (*Chem. & Ind.*, 1955, [25], 701–702).—An apparatus for the detection of colourless zones in paper chromatography or electrophoresis is described. The current from a 1000-kc.p.s. oscillator, regulated by a $0{\cdot}00001$-$\mu$F variable coupling condenser, is fed through an earth-screened cable to one of two metal-foil strips ($1\ cm \times 4\ cm$) forming electrodes mounted on the surface of an ebonite block. The moist chromatographic strip (2·5 cm wide) is sandwiched between thin glass strips ($3\ cm \times 34\ cm$) and the electrodes are moved along the underside of the glass sandwich. A displacement current passes between the electrodes, is rectified by a germanium diode and registered by a micro-ammeter, the reading due to the solvent-damped paper being first set back to zero by means of a zero-shunt. Zones are located by finding max. readings which depend on the impedance of the substance in the zone. By this method zones due to metallic compounds are readily detected. For non-metallic substances, an amplification circuit, in which the germanium diode is replaced by a G.E.T. 1 transistor, is described.

S.C.I. ABSTR.

3263. **Vibrating platinum micro-electrode.** I. P. Alimarin and Z. A. Gallaï (*Zavod. Lab.*, 1955, **21** [2], 244–245).—A platinum micro-electrode, 0·3 mm in diameter and 4 mm long, set in vibration at 50 oscillations per sec. by means of an adapter attached to the usual electric bell, and having an amplitude of 0·5 mm, is shown to be satisfactory for use as an electrode in polarography and amperometric titrations. G. S. SMITH

3264. **New polarographic electrode employing controlled stirring.** P. Arthur, J. C. Komyathy, R. F. Maness and H. W. Vaughan (*Anal. Chem.*, 1955, **27** [6], 895–898).—An apparatus is described in which the solution surrounding a stationary electrode of small diameter is stirred by a revolving tube, the lower end of which surrounds the electrode. With a wax-cooled, mercury-filled electrode tube, polarograms have been obtained in which the curves are reproducible, smooth and easily measurable. Large diffusion currents and very small residual currents are characteristic of the method; the chief drawback is that the electrode surface is not self-renewing. The method may assist in extending the range of polarography to lower concn. and in making it easier to use oscillographic and differential polarography. K. A. PROCTOR

3265. **Application of zero grid-current valve voltmeter to measurement of pH with the glass electrode.** S. Natelson (*Anal. Chem.*, 1955, **27** [6], 1004–1007).—A valve voltmeter has been developed to measure minute voltages through high impedances by using a circuit which eliminates grid current. Its application to pH measurement with the glass electrode is described. K. A. PROCTOR

3266. **The use of simple indicator and reference electrodes in potentiometric titrations in non-aqueous solvents.** H. Zeidler (*Z. anal. Chem.*, 1955, **146** [4], 251–253).—For potentiometric titrations in non-aqueous solvents, with particular reference to amine titrations, the best indicator electrode was Au with a surface area of 1 sq. cm. For the

reference electrode, a special capillary electrode, filled with a soln. of copper acetate in acetic acid, with a carbon rod as conductor, was developed. Other electrodes are discussed and their disadvantages described. R. STERN

3267. **Chromatography combined with automatic recording of electrolytic conductivity. III. Development and tests of the apparatus and of the method.** B. Drake (*Ark. Kemi*, 1955, **8** [2], 159–170).—Improvements of the apparatus for continuous recording of conductivity of solutions from chromatography, etc. (Drake, *Brit. Abstr. C*, 1953, 468), and practical details are described. Conductivity data for the solvents used are quoted and the magnitude of errors caused by capacitative unbalance is discussed. The formula for the interpretation of peak areas in terms of concentration is given, and the correction necessary when resistance and not conductivity is recorded, owing to non-linearity of the relationship, is discussed. A device for the direct recording of conductance and a balancing mechanism without the relays used in the original apparatus are described. An adapter for simultaneous recording with two cells on the same apparatus is described.
E. J. H BIRCH

3268. **Automatic monitor for measuring tritium contamination in air.** D. F. Shaw (*J. Sci. Instrum.*, 1955, **32** [5], 178–180).—A reciprocating pump forces air through an ionisation gauge which is coupled through an electrometer valve to an amplifier. The level of radioactivity can be read directly on a meter or can be continuously recorded. The maximum sensitivity at full scale deflection on the valve voltmeter corresponds to a tritium level of $5 \times 10^{-5}$ $\mu$C per ml, the maximum limit permissible for continuous inhalation. G. SKIRROW

3269. **New time-of-flight mass spectrometer.** H. S. Katzenstein and S. S. Friedland (*Rev. Sci. Instrum.*, 1955, **26** [4], 324–327).—Details are given of a mass spectrometer in which pulses of ions are produced and subjected to time-of-flight analysis. Ionisation potentials obtained with this instrument agree with spectroscopic values to within 0·05 V. G. SKIRROW

3270. **Improved resolving power of the R.F. mass spectrometer by changing the signal shape.** J. Dekleva and A. Peterlin (*Rev. Sci. Instrum.*, 1955, **26** [4], 399).—Improved resolution is obtained by modifying the basic high-frequency signal by the addition of harmonics. G. SKIRROW

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# Notice

The Editor will be pleased to supply on request addresses of authors of papers, if these are available, or of the journals from which abstracts have been prepared.

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# Translations

The following papers of interest to analytical chemists have been translated into English.

CONSULTANTS BUREAU

Copies of these papers can be obtained from Consultants Bureau, 152 West 42nd Street, New York 18, N.Y., U.S.A. Each translation costs $7.50 and orders should state title, author(s) and English page number. The English page number is given in parentheses after the Russian page number.

These translations can also be seen in the library of the Chemical Society, Burlington House, London, W.1.

***J. Anal. Chem., U.S.S.R.—***

The use of oscillographic polarography for the quantitative determination of titanium—Ya. P. Gokhshtein, S. I. Sinyakova and V. D. Yukhtanova, 1954, **9**, 255 (283).

Spectroscopic determination of strontium and lithium in natural waters—T. F. Borovik-Romanova, V. V. Korolev and Yu. I. Kutsenko, 1954, **9**, 265 (295).

Determination of potassium with sodium tetraphenylboron—A. F. Ievinsh and E. Yu. Gudrinietse, 1954, **9**, 270 (301).

Rapid methods of micro-analysis. VIII. Simultaneous micro-determination of carbon, hydrogen and phosphorus in organophosphorus compounds containing C, H, O, P and N—M. O. Korshun, Ev. A. Terentyeva and V. A. Klimova, 1954, **9**, 275 (307).

Energy characteristics and the analytical classification of ions—K. B. Yatsimirsky, 1954, **9**, 282 (315).

Quantitative determination of alkyl-substituted 1-methyl-4-piperidones—A. K. Ruzhentseva and T. D. Pervacheva, 1954, **9**, 304 (337).

Colour reaction of complex formation between elaeostearic acid and picric acid as a qualitative test for tung oil—V. P. Goguadze and T. A. Pkheidze, 1954, **9**, 308 (341).

Spectrographic determination of hafnium and zirconium—E. V. Gusyatskaya and A. K. Rusanov, 1955, **10**, 75 (67).

Quantitative characteristics which determine the possibility of using complex compounds in volumetric analysis—K. B. Yatsimirsky, 1955, **10**, 94 (85).

A volumetric method for the determination of cobalt with dimethylglyoxime—A. K. Babko and M. V. Korotun, 1955, **10**, 100 (91).

The solubility products of the rubeanates of copper, nickel and cobalt—D. P. Malyuga, 1955, **10**, 107 (97).

High-frequency titration. II. Changes in the electrical characteristics of solutions during titration—V. A. Zarinsky and D. I. Koshkin, 1955, **10**, 111 (101).

Determination of caesium as caesium bismuth iodide—V. E. Plyushcehv and V. G. Korshunov, 1955, **10**, 119 (107).

Physico-chemical methods of determining antibiotics. II. The anthrone method for the quantitative determination of mannosidostreptomycin—E. M. Savitskaya, B. P. Bruns, A. A. Korobitskaya and V. D. Kartseva, 1955, **10**, 124 (113).

New Complexones—R. P. Lastovsky, Yu. I. Vainshtein, N. M. Dyatlova, V. Ya. Temkina and N. D. Kolpakova, 1955, **10**, 128 (117).

Luminol indicator paper for hydrogen peroxide detection—A. A. Ponomarenko, 1955, **10**, 132 (121).

Complexones and their significance in analytical chemistry—S. I. Sinyakova, 1955, **10**, 139 (129).

Spectrographic determination of the main components of clay—E. E. Vainshtein, T. V. Borovik-Romanov and V. V. Korolev, 1955, **10**, 158 (147).

A micro method for the determination of primary aromatic amines by potentiometric titration with sodium nitrite—L. M. Litvenenko and A. P. Grekov, 1955, **10**, 164 (153).

Acidimetric determination of phenols—E. T. Lippmaa, 1955, **10**, 169 (157).

Polarographic determination of saccharin—M. B. Neiman, 1955, **10**, 175 (163).

A persulphate - cobalt volumetric method of determining manganese in ores and rocks—D. N. Finkelshtein and I. B. Petropavlovskaya, 1955, **10**, 180 (169).

The use of $(W_1W_2)$-diagrams for X-ray spectrographic analysis—E. E. Vainshtein and I. D. Shevaleevsky, 1955, **10**, 184 (173).

A specific reaction for vanadium—V. L. Zolotavin, 1955, **10**, 189 (177).

Colorimetric determination of the quality of azoribamin—V. M. Iosikova, 1955, **10**, 191 (179).

# ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

| | |
|---|---|
| alternating current | a.c. |
| ampere | amp. |
| Ångstrom unit | A |
| anhydrous | anhyd. |
| approximate, -ly | approx. |
| aqueous | aq. |
| atmospher -e, -ic | atm. |
| boiling-point | b.p. |
| British thermal unit | B.Th.U. |
| calorie (large) | kg-cal. |
| calorie (small) | g-cal. |
| centimetre | cm |
| coefficient | coeff. |
| concentrated | conc. |
| concentration | concn. |
| critical | crit. |
| crystalline | cryst. |
| crystallised | cryst. |
| cubic | cu. |
| current density | c.d. |
| cycles per second | c.p.s. |
| decompos -ing, -ition | (decomp.) |
| density | $\rho$ |
| density, relative | $d$ or wt. per ml |
| derivative | deriv. |
| dilute | dil. |
| direct current | d.c. |
| distilled | dist. |
| electromotive force | e.m.f. |
| electron-volt | eV |
| equivalent | equiv. |
| experiment | expt. |
| foot, feet | ft. |
| gram | g |
| gram-molecule | mole |
| half-wave potential | $E_{\frac{1}{2}}$ |
| horse-power | h.p. |
| hour | hr. |
| hydrogen ion concentration | $[H^{\cdot}]$ |
| hydrogen ion exponent | pH |
| inch | in. |
| infra-red | i.r. |
| insoluble | insol. |
| kilogram | kg |
| kilovolt | kV |
| kilowatt | kW |
| maxim -um, -a | max. |
| melting-point | m.p. |
| microcurie | $\mu$C |
| microgram | $\mu$g |
| microlitre | $\mu$l |
| micron | $\mu$ |
| milliampere | mA |
| millicurie | mC |
| milligram | mg |
| millilitre | ml |
| millimetre | mm |
| millimicron | m$\mu$ |
| millivolt | mV |
| minimum | min. |
| minute (time) | min. |
| molar (concentration) | $M$ |
| molecul -e, -ar | mol. |
| normal (concentration) | $N$ |
| number | no. |
| observed | (obs.) |
| ounce | oz |
| part | pt. |
| patent | pat. |
| parts per million | p.p.m. |
| per cent. wt. in wt. | per cent. w/w |
| per cent. wt. in vol. | per cent. w/v |
| per cent. vol. in vol. | per cent. v/v |
| potential difference | p.d. |
| pound | lb |
| precipitate | ppt. |
| precipitated | pptd. |
| precipitating | pptg. |
| precipitation | pptn. |
| preparation | prep. |
| qualitative, -ly | qual. |
| quantitative, -ly | quant. |
| recrystallised | recryst. |
| refractive index | $n_{\lambda}$ |
| relative humidity | R.H. |
| revolutions per minute | r.p.m. |
| saponification value | sap. val. |
| saturated calomel electrode | S.C.E. |
| second (time) | sec. |
| soluble | sol. |
| solution | soln. |
| specific gravity | sp. gr. |
| specific rotation | $[\alpha]_{\lambda}$ |
| square centimetre | sq. cm |
| standard temperature and pressure | s.t.p. |
| temperature | temp. |
| ultra-violet | u.v. |
| vapour density | v.d. |
| vapour pressure | v.p. |
| volt | V |
| volume | vol. |
| watt | W |
| wavelength | $\lambda$ |
| weight | wt. |

In addition the following symbols are used—

| | | | |
|---|---|---|---|
| greater than | $>$ | less than | $<$ |
| not greater than | $\ngtr$ | not less than | $\nless$ |
| is proportional to | $\propto$ | of the order of, approximately | $\simeq$ |

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, *e.g.*, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cl'$, $SO_4''$. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, *e.g.*, ferric iron becomes $Fe^{III}$ and cuprous copper $Cu^{I}$.

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# ANALYTICAL ABSTRACTS

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